ance of crystallinity occurs at a sharply defined temperature, T_m, in accordance with recent theory.[4] The copolymer acquires a much smaller degree of crystallinity even at lower temperatures and it melts over a much broader range. A well defined melting point for complete disappearance of crystallinity is nevertheless indicated.

Melting points T_m of polyesters varying in chain length, of polyester–diluent mixtures and of various copolyesters and copolyamides have been determined using a micro-melting point apparatus adapted to the observation of the temperature at which the specimen ceases to depolarize transmitted light. The melting points of the copolyamides and certain of the copolyesters depend on the mole fraction of the principal repeating unit in accordance with theory, and are independent of the nature of the co-ingredient. Copolyesters in which the co-ingredient differs from the principal unit only in the number of methylene groups separating the functional groups appear to form mixed crystals, for the melting point depressions are abnormally small in such cases.

As the chain length of decamethylene adipate is decreased $1/T_m$ increases linearly with the reciprocal of the number average number $\bar{x}_n$ of repeating units per molecule, as required by theory. This relationship is the same within experimental error regardless of whether the terminal groups are small (hydroxyl and carboxyl) or large (benzoate, α-naphthoate or cyclohexyl). The previous conclusion that terminal groups will tend to occur outside the crystallites appears to be well founded.

Diluents, including diethyl succinate, diethyl sebacate and benzoquinone, produce increases in $1/T_m$ for decamethylene sebacate which are proportional to the volume fraction of the diluent.

Theoretical relationships permit the calculation of net heats of fusion per gram of crystalline phase from the observed dependences of T_m on each of the above mentioned variables: copolymer composition, chain length and dilution. Values for decamethylene adipate and decamethylene sebacate calculated from the depression in T_m brought about by copolymerization are about 13 to 14 cal. per g. Much larger values are obtained from the dependence of T_m on chain length and from its dependence on dilution with monomeric substances. The source of this discrepancy has not been ascertained. Nevertheless, other results obtained justify further efforts to apply the statistically derived theories to semicrystalline polymers. The influence of foreign units, terminal groups and diluents on the melting of polymers appears to be closely analogous to the classical effects of impurities on solid-liquid equilibria in monomeric compounds.

Exchange Reactions between Cyclohexyl Alkyl Bromides and Chloride Ion[1]

BY ALLEN L. SOLOMON[2] AND HENRY C. THOMAS[3]

The displacement of the halogen of an organic halide by a halide ion has been shown to proceed at a rate representable by a second order law.[4] The mechanism for an alkyl halide has been shown to be that of a Walden inversion.[5] Some investigation has been made of the reduction in reaction rate when the chain of an alkyl halide is branched near the reacting carbon. In this connection much attention has been given to neopentyl bromide.[6] Steric hindrance by alkyl groups to the approach of the halide ion has been offered as an explanation of this effect.[7]

Halide exchange reactions of cyclohexyl chloride and cyclohexyl bromide have been found to be extremely slow as compared to those of the alkyl halides.[3a,5a] The work reported here was undertaken to obtain more information on the effect of the cyclohexyl ring in such reactions. The rates of the reactions between chloride and each of cyclohexyl bromide, bromomethylcyclohexane, β-bromoethylcyclohexane, n-butyl bromide, and isobutyl bromide have been measured. In order to get results which should be nearly comparable as regards the effect of structure, the same solvent and similar concentration and temperature ranges were employed in each case. The solvent used was, by volume, nine parts of acetone and one part of water. Sugden and his co-workers[4b,8] have found several isotopic bromide exchange reactions to be second order in this solvent. We have assumed second order kinetics throughout. The reactions, except in the case of cyclohexyl bromide, are represented by the constants defined in the scheme

$$RBr + Cl^- \underset{k'}{\overset{k}{\rightleftharpoons}} RCl + Br^-$$

(1) This paper is based on the dissertation presented in 1948 by Allen L. Solomon to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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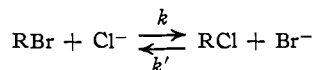
(4) (a) Conant and Hussey, THIS JOURNAL, **47**, 476 (1925); (b) LeRoux and Sugden, J. Chem. Soc., 1279 (1939); (c) McKay, THIS JOURNAL, **65**, 702 (1943).

(5) Hughes, Juliusburger, Masterman, Topley and Weiss, J. Chem. Soc., 1525 (1935).

(6) (a) Bartlett and Rosen, THIS JOURNAL, **64**, 543 (1942); (b) Dostrovsky and Hughes, J. Chem. Soc., 161 (1946).

(7) (a) A. G. Evans, Trans. Faraday Soc., **42**, 719 (1946); (b) Dostrovsky, Hughes and Ingold, J. Chem. Soc., 173 (1946); (c) A. G. Evans, M. G. Evans and Polanyi, ibid., 558 (1947).

(8) Elliott and Sugden, J. Chem. Soc., 1836 (1939).

Lithium chloride has been used as the source of chloride ion.

Experimental

Preparation of Bromomethylcyclohexane.—Commercial cyclohexanol was distilled and converted to cyclohexyl chloride with hydrochloric acid according to directions given by Perlman.[9] Cyclohexyl carbinol was prepared from the chloride by the Grignard reaction with formaldehyde according to a method described in "Organic Syntheses."[10] In the decomposition of the Grignard–formaldehyde complex with ice, the reaction was found to be less violent when the complex was slowly poured on the ice instead of adding the ice to the complex as directed. Cyclohexylcarbinol was converted to bromomethylcyclohexane according to a method described by Hiers and Adams.[11] About a day before a run was to be started the bromide was washed with a 2% sodium carbonate solution, followed by water, dried over anhydrous calcium chloride, and fractionally distilled through a three-foot, half-inch diameter, unpacked column. Immediately before a run the bromide was redistilled and a constant-boiling middle fraction taken: b. p. 60° (8 mm.).

Anal. Calcd. for $C_7H_{13}Br$: C, 47.47; H, 7.40; Br, 45.13. Found: C, 47.67; H, 7.49; Br, 45.04.

Preparation of β-Bromoethylcyclohexane.—Cyclohexyl chloride was prepared by the method cited above. β-Cyclohexylethanol was prepared from cyclohexyl chloride by the Grignard reaction with ethylene oxide according to a method described by Hiers and Adams.[12] The β-cyclohexylethanol was converted to the bromide with a hydrobromic–sulfuric acid mixture according to directions given by Hiers and Adams.[11] The bromide was washed and distilled as mentioned in the previous preparation, b. p. 74° (7 mm.), 75° (8 mm.). *Anal.* Calcd. for $C_8H_{15}Br$: C, 50.27; H, 7.91; Br, 41.81. Found: C, 50.36; H, 7.94; Br, 41.56. Cyclohexyl bromide from the Columbia Organic Chemicals Co., Inc., Columbia, S. C., was washed, dried, fractionated, and redistilled as in the previous preparations, b. p. 57° (18 mm.). Isobutyl and n-butyl bromides from the Eastman Kodak Co. were likewise so treated: isobutyl bromide, b. p. 91°, n-butyl bromide, b. p. 100°.

Preparation of Lithium Chloride.—Lithium carbonate (J. T. Baker Analyzed) was recrystallized from water and treated with concentrated hydrochloric acid in a platinum dish. The solution was filtered. After evaporation to dryness, the lithium chloride was stored over calcium chloride.

Solvent.—Acetone (Mallinckrodt Analytical Reagent) was refluxed over potassium permanganate for several hours, distilled, and dried over anhydrous potassium carbonate. It was then filtered and distilled through a Widmer column and a middle fraction taken. This acetone was diluted with freshly boiled distilled water in the weight ratio 7.011 parts acetone to 1.000 part water, corresponding to a volume ratio of 9.025 parts acetone to 1.000 part of water at 23.8°. The composition of the solvent was known to better than 0.05%.

Equipment and Procedure.—Stock solutions of the inorganic reactant contained about 4 g. of lithium chloride per liter of the solvent. The chloride content of these solutions was determined by the Volhard titration using nitrobenzene to stabilize the end-point. The acetone was removed by boiling before the titration. Determinations on a single solution were consistent to within 0.3%. The content of the various stock solutions differed by no more than 3%.

Corrections to the concentrations of the reactant solutions necessitated by temperature changes were obtained from a graph of the data of Schwers.[13]

The solutions of the reactants were pipetted into glass tubes of about 130 ml. capacity in the shape of inverted Y's. One leg, of about 65 ml. capacity, received 40 ml. of the lithium chloride solution; the other leg, of about 25 ml. capacity, received 10 ml. of the organic bromide solution. The tubes were sealed at a constriction in the neck and immersed in a water thermostat for one and one-half to two hours to reach temperature equilibrium. The thermostat was held at the specified temperature to ±0.02° by conventional mercury regulators and magnetic relays. Thermometers were calibrated to 0.01° by Mr. John A. Gray of this laboratory.

The reactions were started by shaking the tubes. An appropriate time of quenching the reaction was determined from the data of preliminary runs. A tube was removed from the thermostat and placed in an ice-bath, opened, and its contents poured into a separatory funnel containing about 35 ml. of benzene and 40 ml. of water. The reaction tubes were rinsed into the funnels with small portions of water and, after shaking, the layers were separated. The benzene layer was washed three times with water and the aqueous extracts washed with fresh benzene, which in turn was washed with water. No difficulties were experienced with emulsions in the water layer except after washing with fresh benzene. However, by quickly separating most of the water layer, returning it to the benzene layer, and allowing it to stand for a few minutes, the water layer was clarified. A total of about 45 ml. of benzene and 120 ml. of water was used. The combined aqueous extracts were boiled down to about 50 ml. In them inorganic bromide was determined by the BrCN method of Lang.[14] The method of separation was checked by quickly extracting, at room temperature, a mixture of organic halide and lithium chloride solution. Chloride determinations on the separated water layer accounted for all of the lithium chloride introduced. The titration for bromide here gave results insignificantly different from the usual small blank.

At the beginning of a series of determinations a sample was separated immediately after mixing to determine any reaction at very short ("zero") time. Another sample was prepared using pure solvent instead of lithium chloride solution. This sample was treated at the end of the run to determine any side reaction with the solvent.

Before a run the organic bromide was tested for water soluble bromide by adding it to a benzene–water mixture and separating as described. No such bromide was found.

In preliminary runs the total inorganic halide at the completion of the experiment was determined and compared with the initial amount of inorganic chloride. In all cases except that of cyclohexyl bromide it was thus verified that the reaction was an exchange process within about one per cent. Analysis was made by the Volhard method, which was checked on known mixtures of inorganic chloride and bromide and shown to give proper results.

The Lang method, which has been checked by Tomicek and Jansky,[15] was carried out according to the directions given in the literature. It was found essential to stopper the flask while the reaction was taking place. The specified amounts of reagents were found to be sufficient for amounts of bromide less than 0.003 mole. Solutions of sodium thiosulfate were standardized with weights of potassium bromide nearly equivalent to the amounts of bromide found in the samples from the rate determinations. In the standardizations about 0.25 g. of potassium chloride was added. The over-all accuracy of the method was found to be one per cent. or better.

Results and Computation

Table I shows the complete data for two series of determinations. The values of the bromide concentrations have been corrected for the

(9) Perlman, Davidson and Bogert, *J. Org. Chem.*, **1**, 288 (1937).

(10) Gilman and Catlin, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, New York, 1941, p. 188.

(11) Hiers and Adams, THIS JOURNAL, **48**, 2385 (1926).

(12) Hiers and Adams, *ibid.*, **48**, 1089 (1926).

(13) Schwers, *J. chim. phys.*, **9**, 15 (1911).

(14) Lang, *Z. anorg. Chem.*, **144**, 75 (1925).

(15) Tomicek and Jansky, *Coll. Trav. Chim. Tchecoslovaque*, **1**, 585 (1929).

"zero time value" as explained below. The constants for the reactions were determined by first getting approximate values of the constant for the forward reaction, using the equation for the second order irreversible reaction

$$k_1 = \frac{1}{t}\ \frac{x}{\bar{a}(\bar{a} - }$$

TABLE I

(A) RATE DATA FOR ISOBUTYL BROMIDE AND LITHIUM CHLORIDE

Temp., 68.77 ± 0.02°; initial concentrations (moles/liter): RBr, 0.07087[a]; LiCl, 0.07042; volume of sample, 53.41 ml.

	100 [Br⁻][a] m./l.	Time, hr.	100k₁ m./l.[b]	100 [Br⁻] calcd.[c] m./l.
1	0.0848	1.87	9.24	0.0828
2	0.2406	5.50	9.08	0.2378
3	0.7583	18.93	9.03	0.7564
4	1.241	34.30	8.81	1.253
5	1.757	54.22	8.65	1.779
6	2.206	74.47	8.65	2.211
7	2.610	98.13	8.44	2.608
8	2.968	122.05	8.39	2.930
H[d]	0.0399[d]	120.67		

(B) RATE DATA FOR β-BROMOETHYLCYCLOHEXANE AND LITHIUM CHLORIDE

Temp., 55.00 ± 0.02°; initial concentrations (moles/liter): RBr, 0.07100[a]; LiCl, 0.07240; volume of sample, 52.24 ml.

1	0.1283	1.17	21.8	0.1309
2	0.4276	3.98	22.2	0.4278
3	0.8733	8.73	22.1	0.8767
4	1.585	17.98	22.0	1.593
5	2.295	29.60	22.1	2.284
6	2.910	42.83	22.2	2.879
7	3.405	56.92	22.1	3.352
8	3.817	72.95	21.7	3.782
H[d]	0.0417[d]	72.72		

[a] Corrected for zero time value. For the isobutyl bromide run this value was 7.1 × 10⁻⁵ mole Br/liter; for β-bromoethylcyclohexane, 9.09 × 10⁻⁴ mole Br/liter. [b] k₁ calculated from the equation for the irreversible second order reaction. [c] The constants for the equations for the reversible reactions used in calculating these data are: isobutyl bromide, k = 0.0897, k' = 0.0043 (liters/mole hour), β-bromoethylcyclohexane, k = 0.222, k' = 0.0026 (liters/mole hour). [d] Solvent reaction control sample.

in which x is the concentration of liberated bromide, and $\bar{a}$ the average of the nearly equal initial concentrations of the reactants. These values of k_1 are given in Table I. Using them and the equation for the reversible reaction

$$x = \frac{\bar{a}}{1 + \sqrt{k/k'}\ \coth\sqrt{kk'}\ \bar{a}t}$$

good values of k and k' were chosen by trial and error. The value of x is not sensitive to changes in k' in the region investigated; we obtain only rough values for the constant of the reverse reaction. The final selection of constants gives agreement between calculated and observed values of x within two per cent. in most cases.

As has been mentioned the zero time values were determined in each case. These values were quite small except in the cases of bromoethyl- and bromomethylcyclohexane, where titers varied from 0.00022 to 0.00135 mole of bromine per liter. (The blank of the Lang titration amounted to about 0.00003 mole of Br per liter. It has not been subtracted.) In the case of n-butyl bromide the titer was nearly the magnitude of the blank at 40° and increased to 0.00033 mole of Br per liter at 69°. All other values were of the same order as the blank. These results have been provisionally interpreted as being due to a reactive organic halide impurity in the samples of the bromides. (The absence of inorganic halide was demonstrated.) These zero values have been subtracted from all concentrations of bromide used in the rate calculations, the difference being called the observed value of x. The larger titers in the cases of the cyclohexyl derivatives were not used directly; the zero time corrections here were determined by linear extrapolation of the first few results. The possibility has been considered that this effect might be due to an initial unsteady period in the course of the reaction, resulting from a more complex mechanism than that implicitly assumed. There are insufficient data to afford a definite conclusion. In any case the effect is small. Variations in the manner of correcting for it produce differences in the rate constants of the order of the estimated errors of these quantities.

Table II contains the data of the single run made with cyclohexyl bromide and lithium chloride. A Volhard determination of total inorganic halide indicated an increase of 0.00448 mole per liter over the initial amount of inorganic chloride after 5.11 days. A solvent reaction sample showed only 0.000309 mole of bromide reacted in the same time. The data have been represented on the basis of two simultaneous second order reactions.

TABLE II

RATE DATA FOR CYCLOHEXYL BROMIDE AND LITHIUM CHLORIDE

Temp. 68.76 ± 0.02°; initial concentration of cyclohexyl bromide, 0.06957 (moles/liter),[a] lithium chloride 0.06942 (moles/liter); vol. of sample 53.34 ml.

	1000 [Br⁻][a] (moles/ liter)	Time, days	10k[b] (liters/ mole day)	1000 [Br⁻] calcd.[c] k = 0.318
1	0.46	0.240	3.63	0.37
2	1.35	0.862	3.20	1.30
3	2.79	1.88	3.15	2.77
4	4.09	2.83	3.14	4.10
5	5.62	3.90	3.21	5.53
7	7.20	5.10	3.24	7.07
H[d]	0.36	5.08		
7[e]	4.48	5.11		7.07

[a] Corrected for zero time value, 4.7 × 10⁻⁵ moles/liter. [b] Over-all k from second order irreversible equation. [c] Calculated from second order equation for irreversible reaction. [d] Solvent reaction control. [e] Br from total halide determination.

TABLE III

SPECIFIC REACTION RATES AND ACTIVATION FUNCTIONS

$$RBr + Cl^- \xrightarrow{k} RCl + Br^-$$

Substance			$k \times 10^5$ (liters/mole sec.)			ΔF^+ kcal./mole	ΔH^+ kcal./mole	$-\Delta S^+$ cal./ mol.deg.
	40.00	$\pm 0.02°$	55.00	$\pm 0.02°$	68.76 $\pm 0.02°$	Calcd. at 323.18°K.		
n-Butyl bromide	2.15	± 0.04	9.70	± 0.19	35.1 ± 0.7	25.21	20.03	16.0
β-Bromoethylcyclohexane	1.30	± 0.03	6.17	± 0.12	22.1 ± 0.4	25.52	20.29	16.2
Isobutyl bromide	0.122	± 0.002	0.631	± 0.013	2.49 ± 0.05	27.00	21.67	16.5
Bromomethylcyclohexane	0.0886	± 0.0024	0.484	± 0.010	1.97 ± 0.04	27.18	22.30	15.1
Cyclohexyl bromide	68.76°, $k = (3.69 \pm 0.15) \times 10^{-6}$, $k_1 = 1.3 \times 10^{-6}$, $k_2 = 2.3 \times 10^{-6}$ (see text)							

The specific rate constants for the forward exchange reactions appear in Table III. The errors there given are based on the agreement between the observed and the calculated values of x. Experimental errors due to the various operations, such as timing, separation of products, preparation of solutions, temperature control, and analysis, produce effects in the constants small compared to the errors given. The constants given for the cyclohexyl bromide reaction have the following significance: k is an over-all second order rate constant; k_1, a constant for an assumed exchange reaction k_2, a constant for the elimination of bromide unaccompanied by exchange. In preliminary work with a dioxane–water solvent this same increase in halide ion content of the solution was observed to an even greater extent. No serious attempt has been made to interpret these results.

Discussion

The data of Table III have been used to compute the constants in the Arrhenius equation

$$\ln k = \ln A - E/RT$$

A maximum error of 600 cal./mole may be assigned to the energy of activation, E. Calculated values of the rate constants using these values of E and $\ln A$ agree with the experimental values within one per cent. Using the average values of the Arrhenius constants, values of $\ln k$ at 323.18°K. were used to find the thermo-dynamic functions of the activated complex.[16] These also appear in Table III.

We have attempted to correlate the results of this work with the structure of the compounds studied. Interesting regularities appear if one assumes additivity of the Arrhenius activation energy in terms of contributions from carbon atoms as determined by their positions in the skeleton with respect to the substituent halogen. The accuracy of the data does not, however, warrant a detailed discussion, particularly in the absence of any guiding theory.

The marked effect on the velocity due to branching at the β-carbon is quite apparent in the cases studied.

Summary

The specific rate constants and the thermodynamic functions of activation have been determined for the exchange reactions of n-butyl bromide, β-bromoethylcyclohexane, isobutyl bromide, bromomethylcyclohexane with lithium chloride in a nine-to-one acetone–water solution over a temperature range from 40 to 69°. Some qualitative information has been obtained on the reaction of cyclohexyl bromide with lithium chloride.

(16) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.