It is clear that more work, both structural and theoretical, is needed to resolve the questions still surrounding the substituent–cyclopropane interaction. One attack is to compare structures of identical substitution where θ is fixed at 0 and 90°. Such studies are currently in progress.

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Supplementary Material Available: Tables II and V, which list the structure amplitudes for each structure (19 pages). Ordering information is given on any current masthead page.

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The Effects of Solvent–Solute Interactions on the Stereochemical Course of the High-Energy Chlorine-38 for Chlorine Substitution Process in Diastereomeric Dichloroalkanes in the Condensed Phase[1]

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Abstract: The stereochemistry of the high-energy chlorine-38 for chlorine substitution process was studied in diastereomeric 2,4-dichloropentane and 2,3-dichlorobutane in solutions. The experimental results indicate that the stereochemical course of the substitution process is predominantly and directly controlled by the properties of the solvent molecules, specifically by the dielectric constant, which in turn is responsible for the magnitude of intermolecular interaction between reactants and solvents. It appears that strong intermolecular interaction favors substitution via retention of configuration, whereas in solvents having a low dielectric constant the retention/inversion ratio decreases.

The role of solvents in determining the relative distribution and nature of reaction products in high-energy reactions, e.g., in photochemical or hot atom reactions, where the reactants are not in thermal equilibrium with the environment is still not completely understood and only relatively few studies have addressed themselves to this problem.[2-3] An especially instructive case for the evaluation of such solvent effects appears to be the investigation of those high-energy reactions which lead to substitution products either via retention or inversion of configuration, as, e.g., the ^{38}Cl for Cl substitution in diastereomeric molecules such as *meso*- or *dl*-2,3-dichlorobutane. In these reactions the kinetically excited ^{38}Cl is usually generated as a result of a nuclear process such as ^{37}Cl(n,γ)^{38}Cl.[3-10]

While in the gas phase the above "hot" substitution reaction leads overwhelmingly to the substitution product formed under retention of configuration,[4-8] more recently Stöcklin et al.[3] demonstrated that the stereochemical course of the ^{38}Cl for Cl substitution in these systems can be drastically influenced by the nature and concentration of the solvent present in the reaction mixture if the reaction is carried out in the condensed phase. These authors correlated the stereochemical course of the reaction to the relative concentrations of the sterically different rotational isomers, which vary as a function of solvent nature and concentration, and for which they assume different reaction cross sections for substitution with retention or inversion of configuration. On the basis of the observed conformational effect and some additional evidence these authors suggest that the substitution occurs via a one-step mechanism, in which the relative concentration of the conformers and their relative accessibility for front- or back-side attack by the substituting agent, leading to substitution via retention or inversion, respectively, determine the overall course of the reaction. This mechanism is distinctly different from the two-step caged radical-radical recombination mechanism (Frank Rabinowitch caging) which was previously invoked to rationalize the decrease of stereospecificity observed when these reactions are carried out in the condensed state.[4-5]

$$RX + Y^* \rightarrow [RY]^* \rightarrow [R\cdot + Y\cdot] \rightarrow RY$$

$$\text{or} \quad RX + Y^* \rightarrow [X\cdot + R\cdot + Y\cdot] \rightarrow RY + X\cdot$$

According to the latter mechanism the ^{38}Cl for Cl replacement followed by a breakup of the molecule and recombination of the resulting radicals may occur via retention or inversion of configuration.

While in the former case the solvent properties determine (indirectly) the course of reaction by governing the conformer concentrations, in the case of the caged radical-radical recombination mechanism the solvent properties will be directly responsible for the product yields and their distribution by controlling the recombination efficiency of the radicals in the solvent cage. Specifically, in the case of the diastereomeric dichlorobutanes the stereochemical course of the substitution may depend strongly on whether or not the organic radical can achieve planarity before recombination with the ^{38}Cl occurs, a process which may be strongly influenced by solvent properties, such as solvent mass, molecule size, viscosity, and interaction energy between solvent and radical.

Since a considerable fraction of chemical reactions occurring in solution involves radicals or other highly energetic species it seems that the information which can be obtained by studying the dependence of product yields and distribution in these high-energy reactions can also greatly enhance the understanding of the mechanisms by which solvents influence the course of reaction in less energetic processes as in photochemistry or radical reactions in general. Thus the present investigation was started with the following objectives in mind:

(1) Since the "conformational effect" has so far been observed only in one system,[3-10] i.e., 2,3-dichlorobutane, with a very limited number of solvents present, it seemed imperative to establish whether such conformational effects are a general feature of "hot" halogen substitution reactions.

For this reason we have examined the studies to a greater variety of solvents and included the 2,4-dichloropentane system into our investigation.

An additional feature of the diastereomers of the 2,4-dichloropentane is that in contrast to the 2,3-dichlorobutane system, where the two chlorine atoms are in vicinal positions, in 2,4-dichloropentane the chlorine atoms are separated by a methylene group, which would suppress the formation of three-centered bond structure of the type

which may control to a certain extent the stereochemistry of the reactions[11] in the 2,3-dichlorobutane systems.

(2) Secondly, in order to separate the conformational effect from other (direct) solvent effects the stereochemistry of the high-energy ^{38}Cl for Cl substitution should be studied in a system where the conformational composition of the reaction mixture is not significantly changed by the nature of the solvent. Such a system is again the diastereomeric 2,4-dichloropentanes where theoretical calculations as well as previous experimental work[12] strongly suggest that each diastereomeric 2,4-dichloropentane system has one preferred conformer with only minor amounts of other conformers present, and what is more important that the relative conformer population is not affected to any significant degree by the nature of the solvent.

Thus, if a strong solvent dependence of the ratios of the radiochemical yields of the products via chlorine-38 for chlorine substitution under retention or inversion of configuration in these latter systems is observed, it cannot be solely explained by conformational effects and would indicate the importance of other solvent parameters on the stereochemical course of the substitution process.

The experiments described in the following exhibit indeed a pronounced solvent dependence as a function of the concentration and nature of the solvent and an attempt has been made to correlate the observed effects with various physical and chemical properties of the solvent molecules in order to gain further insight into the detailed chlorine-38 for chlorine substitution mechanisms in the condensed phase.

Experimental Section

A. Materials. A diastereomeric mixture of 2,3-dichlorobutane (DCB) was obtained from Aldrich Chemical Co. A mixture of the diastereomeric 2,4-dichloropentanes (DCP) was prepared by adding thionyl chloride to 2,4-pentanediol at 0 °C following the procedure published by Pritchard et al.[14] 2,4-Pentanediol was purchased from Aldrich Chemical Co. with 99% purity.

The meso and *dl* forms of DCB and DCP were separated by gas chromatography, utilizing a 25-ft stainless steel column (¼ in. i.d.) with 15% Igepal CO-800 on Chromosorb W AW, 60-80 mesh at 65-80 °C, helium flow 80 mL/min.

The solvents used in this study were obtained from various companies and dried and purified when necessary.

Iodine was obtained from Aldrich Chemical Co. and bromine was purchased from J. T. Baker Chemical Co. with a 99.8% purity and used without further purification.

B. Sample Preparation and Irradiation. Samples were prepared for neutron irradiation by introducing the desired amount of meso or *dl* compound and various amounts of solvent together with about 2 mol % of I_2 as scavenger, an amount which was found sufficient to suppress thermal diffusive reactions, into quartz ampules with a volume of 0.3-0.4 mL. The amount of DCB or DCP used in these experiments was about 15 mg. Samples were thoroughly degassed under vacuum, sealed, and immediately subjected to neutron irradiation.

The neutron irradiation was carried out at the VPI & SU nuclear reactor with a neutron flux of 1.3×10^{12} n cm^{-2} s^{-1} for 2-5 min at 40 °C. In the case of low-temperature irradiations the samples were kept in liquid nitrogen at −196 °C during this procedure.

C. Sample Analysis. The irradiated samples were transferred to a vial containing about 1 mL of ether and 0.5 mL of a 10% aqueous solution of a 1:1 mixture of Na_2SO_3 and Na_2CO_3. The organic layer was separated, transferred to another vial, washed with distilled water, and dried with Na_2SO_4. After a mixture of inactive carriers was added the organic products were subsequently analyzed by gas chromatography. Several columns were used in this study: a 35-ft stainless steel column (¼ in. i.d.) with 15% DEGS on Chromosorb W AW, 60-80 mesh at 75 °C, helium flow 80 mL/min for the separation of the products formed in the irradiation of DCP; a 25-ft stainless steel column (¼ in. i.d.) with 15% Igepal CO-800 on Chromosorb W AW, 60-80 mesh at 70 °C and 80 mL/min He flow; and a 35-ft stainless steel column (¼ in. i.d.) with 15% DEGS on Chromosorb W AW, 60-80 mesh at 65 °C, 80 mL/min He flow, was used for product separation in the DCB system.

D. Radioactivity Assay. The chlorine-38 labeled products separated by gas chromatography were adsorbed on charcoal directly from the effluent gas stream. The radioactivity of the products was subsequently measured in a well-type scintillation counter. Appropriate decay corrections were made and the ratio of retention to inversion was determined by direct comparison of the radioactivity incorporated in the compound formed following chlorine-38 for chlorine substitution under retention of configuration to that observed in the compound formed under inversion of configuration.

E. Conformational Analysis. The relative conformer distributions of *meso-* and *dl*-DCB solutions in *n*-pentane, cyclohexane, and methanol were previously determined by Stöcklin et al.[3]

In the case of *meso*-DCP earlier work[15-18] suggested the presence of only one form, namely, the TG conformer. Calculations using the "staggered approximation" predicted the relative energies for the next stable conformers to be (kcal/mol) 18.6 for TT, 39.4 for TG′, and 402 for GG.[19] From these values it appears that the addition of solvents would have no significant effect on the relative conformer concentrations. This is in line with the results[17-19] of IR investigations of the pure liquid and in cyclohexanone which did not reveal any noticeable changes in the IR spectra, a result which was further supported by NMR studies of the pure liquid DCP and DCP solutions in CCl_4 and chlorobenzene.[15]

However, more recent NMR and IR investigations[13] of *meso*-DCP revealed in addition to TG the possible existence of other conformers such as TT, TG′, and GG, whose energies (relative to TG) were calculated to be (kcal/mol) TT 2.9, TG′ 1.7, and GG 2.8.[19] A similar situation prevails in the *dl*-2,4-dichloropentane system. Here the preferred conformers are the TT and GG forms with small amounts of TG conformer present. (Very small amounts of form GG′ cannot be excluded.) The relative energies for these conformers were semiempirically calculated (kcal/mol) for TT 0, GG 1.5, and TG 2.5.

A *quantitative* experimental determination of the conformer concentrations by means of NMR or IR techniques is very difficult because of the relatively large number of conformers to be considered in the evaluation of these spectra.

We, therefore, attempted to estimate the solvent effects on conformer population from semiempirical calculations based on Onsager's theory.[20-22]

The relative distribution of two conformers (N_I and N_{II}) in a solution can be calculated from the equation

$$N_I/N_{II} = (f_I/f_{II}) \exp(-\Delta E_{I/II}{}^{\text{solution}}/RT) \qquad (1)$$

where f_I/f_{II} is the ratio of the partition functions of the two conformers. It is usually approximated to be unity.[21] $\Delta E_{I/II}{}^{\text{solution}}$ is the energy difference between the two rotational isomers in the solution. R is the gas constant and T the absolute temperature. $\Delta E_{I/II}{}^{\text{solution}}$ can be obtained from the relation

$$\Delta E_{I/II}{}^{\text{solution}} = \Delta E_{I/II}{}^{\text{gas}} - \frac{\epsilon - 1}{2\epsilon + 1}\,\frac{\mu_I{}^2 - \mu_{II}{}^2}{a^3} \qquad (2)$$

$\Delta E_{I/II}{}^{\text{gas}}$ is the energy difference between the two conformers in the gas phase. (A more elaborate equation for $\Delta E_{I/II}{}^{\text{solution}}$ was established by Abraham et al.,[23] who took into account the polarizability of the solvent and multipole interactions between solute and solvent molecules.) ϵ is the dielectric constant of the solution, $\mu_{I/II}$ the dipole moments of the two rotamers, and a^3 the molecular volume of the solute molecule. The dielectric constants were obtained from ref 24. The molecular volume a^3 of DCP can be obtained in the usual manner from its molecular weight, its density, and Avogadro's number.

The appropriate $\Delta E_{I/II}{}^{\text{gas}}$ values can be found in ref 19. The dipole moments of the various conformers were approximated from the structure of the conformers[25] by considering the bond angles as tetrahedral and the dipole moments for the C-Cl bond = 1.85 D, C-CH_3 = −0.4 D, and C-H = 0 D. This approximation resulted in the following dipole moments for the various conformers (all in D): *meso*-DCP, TG 2.60, TT 3.98, TG′ 2.20; *dl*-DCP, TT and GG 2.60, TG′ 3.98, TG 2.20.

Table I. Estimated Dipole Moments and Relative Conformer Concentrations in Solutions of *meso-* and *dl*-2,4- Dichloropentane (10 mol %) in Methanol, Cyclohexane, and Me_2SO

		Conformer population, %			
Conformers	μ calcd,[a] D	In 90% methanol[a]	In 90% cyclohexane[a]	In 90% Me_2SO[b]	In Me_2SO[c]
meso-DCP					
TG	2.60	91.5	93.9	87.8	86.3
TT	3.98	5.1	1.6	7.3	7.6
TG′	2.20	3.4	4.4	5.0	4.3
dl-DCP					
TT	2.60	91.8	91.6	88.6	86.4
GG	2.60	7.3	7.3	9.8	7.1
TG	2.20	0.9	1.1	1.6	4.9
TG′	3.98	Not considered			

[a] This work (conformer concentration calculated for 25 °C). [b] This work (conformer concentration calculated for 70 °C). [c] Data from ref 26 (conformer concentration at 70 °C in Me_2SO in presence of LiCl).

By substituting these parameters into eq 1 and 2 the concentration of various conformers can be estimated as a function of the solvents with a wide range of dielectric constants.

It can be easily shown that on the basis of these calculations only slight changes in the conformer distribution can be expected, e.g., in methanol solution (ϵ = 32.63) of the *dl* isomer the relative concentrations are C_{TT}:C_{GG}:C_{TG} = 91.8:7.3:0.9, whereas in cyclohexane, which has a much lower dielectric constant (ϵ = 2.2), the corresponding values are 91.6:7.3:1.1. Similar results are obtained in the meso system (Table I).

An independent check of the validity of these calculations can be derived from the work by Flory and Williams,[26] who, based on the statistical weight parameters obtained in the stereochemical equilibration of 2,4-DCP in Me_2SO, calculated the following major conformer populations for the *dl* isomer in Me_2SO at 70 °C: TT 86.4%, GG 7.1%, TG 4.9%, and for the meso isomer, TG 86.3%, TT 7.6%, TG′ 4.3%. By using the appropriate dielectric constant for Me_2SO (41.6) and ΔE^{gas} values and our estimated values for the dipole moments of the various conformers (vide supra) we would obtain from eq 1 and 2 the following conformer concentrations under the experimental conditions: *meso*-DCP, TG 87.7%, TT 7.3%, TG′ 5.0%; *dl*-DCP, TT 88.6%, GG 9.8%, TG 1.6%. The good agreement between these data (see also Table I) seems to support the validity of this approach.

From these results it again appears that the presence of solvents with widely different dielectric constants has only a negligible effect on the relative amounts of the preferred form present in the mixture and significant changes can be expected solely in the ratios of the conformer population of the two minor components, e.g., GG and TG, if *dl*-DCP is the substrate, where the ratios change from approximately C_{GG}:C_{TG} = 8.1 in methanol to 6.6 in cyclohexane.

Results and Discussion

In Figure 1 the retention to inversion ratios, i.e., the ratios of the radiochemical yields of the chlorine-38 labeled 2,4-dichloropentanes (DCP) formed via chlorine-38 for chlorine exchange under retention of configuration (meso) to the product formed under inversion of configuration (*dl*), are plotted as a function of mole fraction additive for the various solutions containing *meso*-2,4-dichloropentanes. Figure 2 shows a similar plot of the results obtained with *dl*-2,4-dichloropentane as the substrate. In this case *meso*-DCP is the product formed under inversion of configuration, whereas *dl*-DCP is the result of substitution via retention of configuration.

In agreement with the results previously observed in the 2,3-dichlorobutane system[3,10] the addition of bromine causes a drastic increase in the retention/inversion ratios, which is also true to a lesser degree in the case of other solvents such as

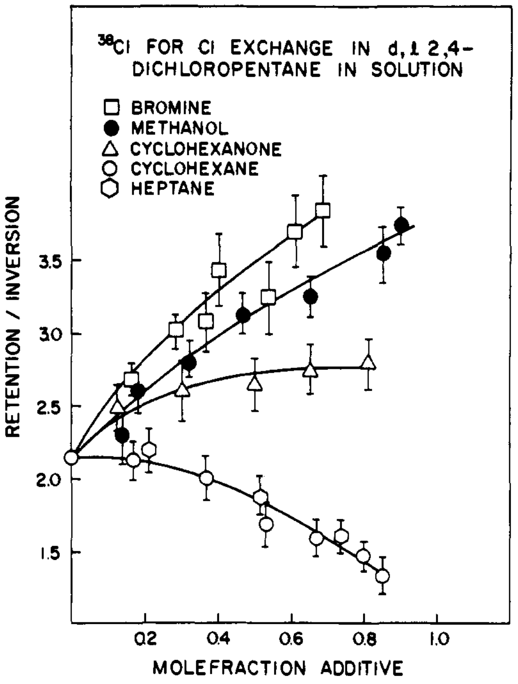

Figure 1. Solvent dependence of the ratio of retention to inversion following the chlorine-38 for chlorine substitution in solutions of *dl*-2,4-dichloropentane (at 25 °C).

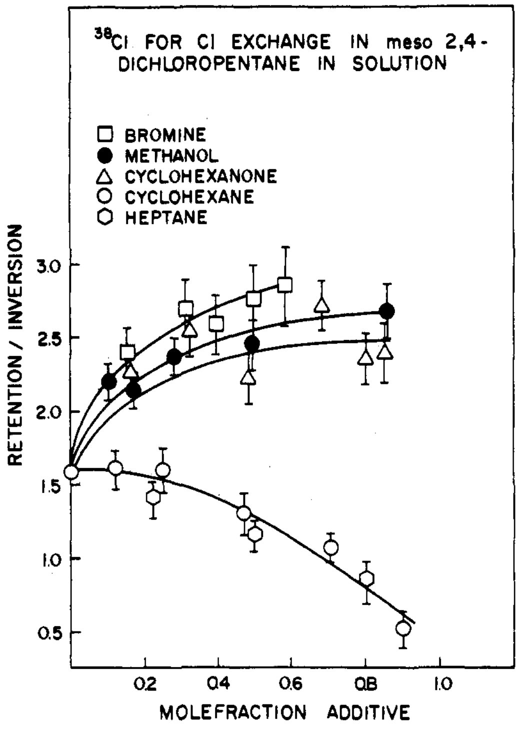

Figure 2. Solvent dependence of the ratio of retention to inversion following the chlorine-38 for chlorine substitution in solutions of *meso*-2,4-dichloropentane (at 25 °C).

methanol, cyclohexanone, and acetonitrile, whereas cyclohexane and *n*-heptane reduce this ratio below the value observed in the pure liquid *meso*- or *dl*-2,4-dichloropentanes, respectively.

Since the available experimental evidence as well as theoretical considerations (see Experimental Section) lead to the conclusion that the relative conformer concentration is not significantly affected by the presence of solvents with different dielectric constants, it is obvious that the observed solvent dependence of the retention to inversion ratios in the DCP systems cannot be correlated with the conformational composition of the reaction mixture.

This conclusion is further supported by the results observed in experiments in which the neat diastereomers of DCB in crystalline form at −196 °C were subjected to neutron irradiation. Since in the solid (crystalline) state only the most stable rotamers are present,[27] one should expect distinct changes in the experimental results in the DCB system if one goes from the liquid state (room temperature) where several conformers are present in equilibrium to the solid state (at −196 °C). However, in these experiments only small changes in the retention/inversion ratios compared with that obtained in the liquid state could be observed, e.g., *dl*-DCB, liquid 2.78, solid 2.57; *meso*-DCB, liquid 2.45, solid 2.21. These slight differences could be attributed to the concomitant variations of the dielectric constants with temperature. If conformational changes would be responsible for this result an opposite trend in the retention/inversion ratios should be observed in the case of *dl*-DCB.

Thus in the following other parameters which could be responsible for the drastic changes inflicted upon the stereochemistry of the chlorine-38 for chlorine substitution in dichlorinated alkanes by the various solvents will be discussed.

In our effort to correlate the retention/inversion ratios to the physical and chemical properties of the solvent present we extended the investigation to a large number of different solvents and studied the solvent effect in both the diastereomers of 2,3-dichlorobutane and 2,4-dichloropentane. In each case the experiment was carried out at room temperature in a solution containing 90 mol % solvent in presence of a sufficient amount of I_2 as scavenger.

The dependence of the observed retention/inversion ratios on several molecular parameters of the solvents, such as density, surface tension, viscosity, polarization, dipole moment, polarizability, ionization and first excitation potentials, molecular diameter, and dielectric constants, was considered. Among these parameters only the latter property of the solvents showed a reasonably smooth correlation with the experimental data.

For comparison the retention/inversion ratios observed in solutions of *dl*-2,3-dichlorobutane and *dl*-2,4-dichloropentane are shown in Figure 3 as a function of $(\epsilon - 1)/(2\epsilon + 1)$. A similar plot for the corresponding meso systems can be found in Figure 4.

Both figures show generally a smooth correlation between the inversion/retention ratios and $(\epsilon - 1)/(2\epsilon + 1)$ for most of the solvents studied. However, it is also quite obvious that this correlation does not hold when Br_2 is used as solvent.

The physical significance of the parameter $(\epsilon - 1)/(2\epsilon + 1)$ is that it can be related to the magnitude of the intermolecular interaction between the reactants and the surrounding solvent molecules. An estimate of the magnitude of these interactions may be obtained from the free-energy change which occurs when a solute or solvent molecule is taken from the solution out into gas. This free-energy change[28] is mainly controlled by two terms: the cavity term, which is a function of surface tension, and perhaps more importantly by the interaction term which is related to the dipole and multipole moments of the solute molecule, its molecular volume a^3, and the term $(\epsilon - 1)/(2\epsilon + 1)$.

Thus, if the magnitude of interaction between solute and solvent molecules can indeed be represented by this free-energy change, one might expect to see for a given solute molecule a correlation between individual product yields or as in this case between the retention to inversion ratio and $(\epsilon - 1)/(2\epsilon + 1)$, if one neglects the higher multipole interactions and the cavity effect.[29] Such a correlation is clearly borne out in Figure 3 for

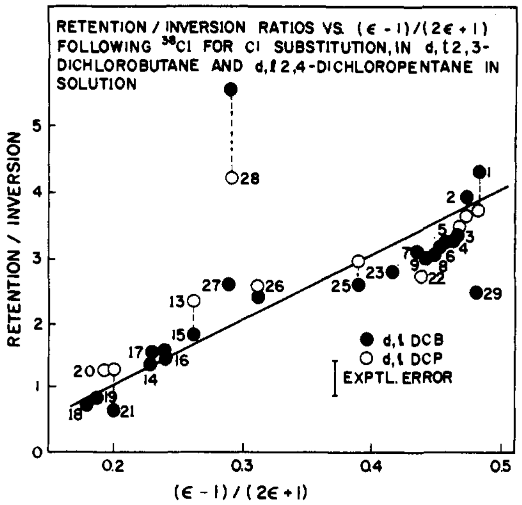

Figure 3. Retention/inversion ratios observed in solutions of *dl*-2,3-dichlorobutane and *dl*-2,4-dichloropentane as a function of (ε − 1)/(2ε + 1) (ε = dielectric constant of solvent): (1) methanol, (2) ethanol, (3) 1-propanol, (4) 2-propanol, (5) 1-butanol, (6) 2-butanol, (7) 2-methyl-2-propanol, (8) 1-pentanol, (9) 1-hexanol, (10) 1-heptanol, (11) carbon tetrachloride, (12) nitrobenzene, (13) carbon disulfide, (14) benzene, (15) toluene, (16) ethylbenzene, (17) *tert*-butylbenzene, (18) *n*-pentane, (19) *n*-hexane, (20) *n*-heptane, (21) cyclohexane, (22) cyclohexanone, (23) *dl*-DCB, (24) *meso*-DCB, (25) acetic acid, (26) propanoic acid, (27) butyric acid, (28) Br_2, (29) acetonitrile, (30) 2-methyl-2-propanol.

the *dl* diastereomers of 2,3-dichlorobutane and 2,4-dichloropentanes, and to a lesser degree in Figure 4 for the corresponding meso systems.[30]

Although the experimental evidence unambiguously indicates that the stereochemical course is not controlled by the conformational composition of the reaction mixture, it does not rule out the possibility of a hot one-step reaction mechanism which may involve a direct replacement step or a "caged complex".[31] An interpretation of the experimental results in terms of a hot one-step mechanism, however, is made difficult by the inherent deficiency of these kinds of solution experiments which do not allow a meaningful determination of the absolute radiochemical yields of the two reaction products.[33] Since only the retention/inversion ratio can be measured it is not clear whether the variation in these ratios is caused by an increase of the yield of the retained form or by a reduced formation of the inverted product or by both. However, one might want to invoke an analogy to similar systems, such as the diastereomeric 1,2-dichloro-1,2-difluoroethanes,[9] where density variation studies indicated that the reaction channel leading to inverted product is low energy[34] and probably because of steric hindrance less efficient, while the yields of the retained product increase monotonically with increasing density, owing to more efficient excitation-stabilization at higher density of the higher energy reaction channel yielding the retained product.

The fact that the retention to inversion ratio increases with (ε − 1)/(2ε + 1) could then be interpreted by assuming that in those cases where the reactants interact strongly with the surrounding solvent molecules, the excess energy of the retained product formed in a hot one-step substitution at higher energies is quickly dissipated and the product stabilized, whereas in those solvents which have a low dielectric constant, the energy dissipation proceeds less rapidly and less of the retained product formed in a high-energy substitution becomes stabilized. Thus, the retention/inversion ratio remains small or even drops.

Alternatively, in terms of the immediate caged radical-radical recombination of the type

$$RX + Y^* \rightarrow [RY]^* \rightarrow R + Y \rightarrow RY$$

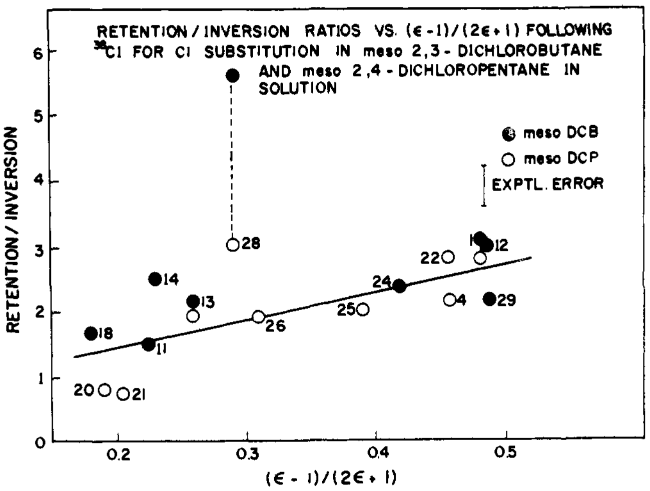

Figure 4. Retention/inversion ratios observed in solutions of *meso*-2,3-dichlorobutane and *meso*-2,4-dichloropentane as a function of (ε − 1)/(2ε + 1) (ε = dielectric constant of solvent). (Solvents: see Figure 3.)

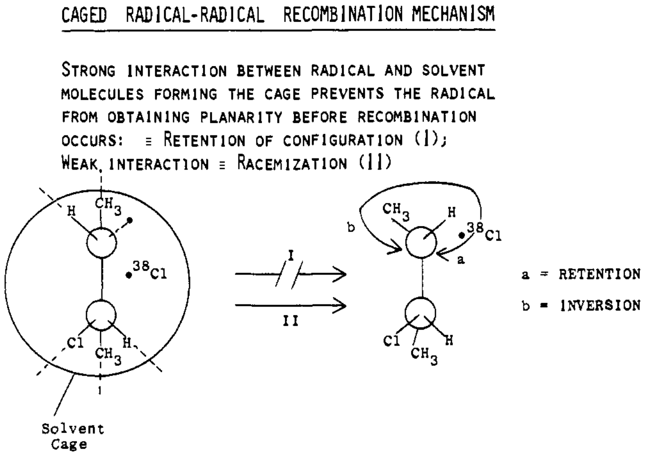

Figure 5. Schematic presentation of the consequences of solvent–radical interaction on the stereochemical course of the ^{38}Cl for Cl substitution process assuming a caged radical–radical recombination mechanism.

recombination following chlorine-38 for chlorine displacement and subsequent breakup of the excited intermediate may occur via both retention or inversion of configuration. In the case of strong interaction between the intermediate radical and the surrounding molecules the radical will most likely not achieve planarity before recombination takes place and recombination will occur resulting in a labeled molecule which maintains the configuration it obtained in the primary step, the direct displacement process. (See Figure 5.) The results in Figures 3 and 4 which show a drastically higher retention/inversion ratio for strongly interacting solvents would thus indicate that the primary step is the substitution via frontside attack leading to retention of configuration.

In the case of weakly interacting solvents some equilibrium concentration of *dl* and meso product may eventually be reached. If one considers the values found in *n*-pentane, *n*-hexane, *n*-heptane, or cyclohexane solution of these various systems as indicative of this equilibrium distribution, the following approximate equilibrium populations should exist: *meso*-DCB, 60%; *dl*-DCB, 40% (calculated from an average retention/inversion ratio of 0.77 found in the *dl*-DCB system and an average retention/inversion rate of 1.7 observed in *meso*-DCB solutions of the above solvents). They are very similar to the product distribution obtained in the photochlorination of 2-chlorobutane.[35] The corresponding values for DCP are *meso*-DCP, 43%; *dl*-DCP, 57% (calculated from an

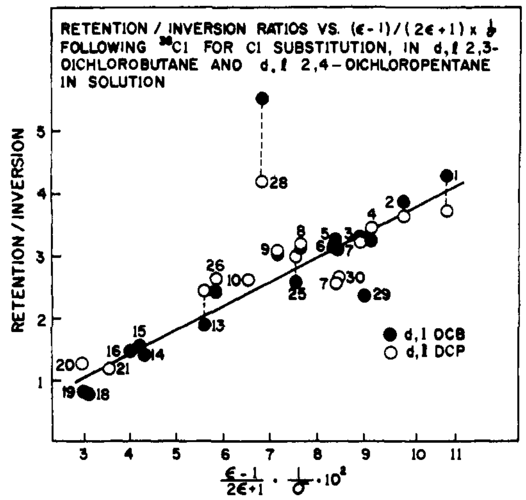

Figure 6. Retention/inversion ratios observed in solutions of *dl*-2,3-dichlorobutanes and *dl*-2,4-dichloropentanes as a function of $(1/\sigma)(\epsilon - 1)/(2\epsilon + 1)$. (Solvents: see Figure 3.)

average retention to inversion of 1.25 found in *dl*-DCP and 0.75 in *meso*-DCP in these solvent systems). These numbers also compare favorably with the equilibrium concentration previously observed by Flory et al.:[26] *meso*-DCP, 36.4%; *dl*-DCP, 63.7%. The strong deviations observed in the presence of the highly reactive Br_2 as solvent are probably not the result of the physical properties of this "solvent" but they appear to be the consequence of a chemical interference with the reactant (chemical suppression of one reaction channel by the Br_2 channel).[36]

Although the dependence of the stereochemical course of the ^{38}Cl for Cl substitution process on the interaction energy has been clearly demonstrated in this study, the complexity of the interactions may require further improvement of the parameters used to correlate the retention/inversion ratios to the interaction energy term.

As shown in Figure 6, where the retention/inversion ratios for *dl*-DCB and *dl*-DCP are plotted as a function of $(1/\sigma)(\epsilon - 1)$, one such additional term appears to be the molecular diameter,[38] σ, of the solvent. Experimental work to assess the implications of these results is presently being carried out in this laboratory.

Conclusion

Although the experimental results presented in this study are consistent with both a hot one-step substitution mechanism and the caged radical-radical recombination model and thus do not allow any conclusive distinction between these two mechanisms, they clearly indicate that the stereochemistry is predominantly and *directly* governed by the properties of the solvent and not by an indirect solvent effect on the relative rotamer populations of the substrate molecule. The parameters most likely responsible are related to the intermolecular interactions between reactants and the surrounding solvent molecules; they are in particular the dielectric constant and to a minor extent the size of the solvent molecules.

In terms of the hot one-step substitution mechanism the strong interaction between solvent and reactants may enhance a rapid transfer of excitation energy and thus excitation-stabilize the product formed via retention of configuration whereas in terms of the caged radical-radical recombination model the strong solvation will prevent the intermediate radical from obtaining planarity and recombination will result in a labeled molecule having the same configuration as the product formed in the primary displacement step (retention).

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(1) Work supported by the U.S. Atomic Energy Research and Development Administration.

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(29) It should be pointed out that eq 2, which was used for the calculation of the conformer concentration in the Experimental Section, contains similar interaction terms. However, the conformer concentration is determined by the energy *difference* of the two conformers in the solution, $\Delta E_{I/II}^{solution}$, which in turn depends on the *difference* of the energies of the two conformers in the gas phase, $\Delta E_{I/II}^{gas}$, and the *difference* of the interaction energies of the two conformers in the solution, $(\epsilon - 1)/(2\epsilon + 1)[(\mu_I^2 - \mu_{II}^2)/a^3]$. It can easily be seen that in a system of conformers where $\Delta E_{I/II}^{gas}$ is relatively large and $(\mu_I^2 - \mu_{II}^2)$ relatively small, as it happens to be in the case of DCP, $\Delta E_{I/II}^{solutions}$ and consequently the relative conformer concentrations do not change significantly even if ϵ, the dielectric constant of the solvent and thus the absolute interaction energy between solvent and solute, i.e., the term $(\epsilon - 1)/(2\epsilon + 1)$, μ^2/a^3, is drastically altered. This different dependence of conformer composition and solvent–solute interaction upon variation of the dielectric constant of the solvent was used in the present investigation to separate the conformational effect from other solvent effects.

(30) An explanation for the less pronounced dependence of the retention/inversion ratio on the interaction energy in the meso system compared with the corresponding values for the *dl* diastereomers may be seen in the fact that in the case of the meso isomer a smaller number of the primary ^{38}Cl for Cl replacement events leading eventually to substitution occur via frontside attack to give the retained product than in the *dl* isomer. Thus even in the presence of strongly interacting solvents the retention/inversion will remain relatively small as compared with the *dl* system. Alternatively, in terms of the caged radical–radical recombination model, one can argue that the radical formed by the breakup of the (excited) meso ^{38}Cl product shows less interaction with the surrounding solvent molecules and therefore achieves planarity more easily than the corresponding radical formed by the fragmentation of the (excited) *dl* ^{38}Cl product.

(31) A hot one-step substitution process which involves a collision complex which is collisionally stabilized and has a lifetime sufficiently long to allow inversion of configuration ("direct replacement with collisional stabilization of the caged complex" model) has been recently postulated by Stöcklin et al.[9] Additional evidence supporting the "caged complex" model was presented by Rack et al.[32] in their study of the reactions of "hot" iodine species with acetylene.

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(33) Absolute radiochemical yields of the retained or inverted product can be obtained only in the neat systems. In the solutions the solvent molecules will compete with the solute for "hot" ^{38}Cl atoms and react with them under formation of a variety of products. It is clearly impossible to identify all these products resulting from the reactions of ^{38}Cl with solvent or solute, respectively, a requirement necessary for the determination of the absolute (radiochemical) yields of the substitution products obtained via retention or inversion of configuration.

(34) An explanation for the fact that the reaction channel leading to inverted product is low energy could be derived by considering the time required for the inversion process to occur. Since the inversion is a relatively slow process only low energy ^{38}Cl will remain long enough in the vicinity of the substrate molecule to react with the substrate after inversion has occurred.

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(36) It has been postulated that the ^{38}Cl formed as a result of the breakup of the primary reaction products is immediately scavenged via H abstraction from one of the solvent molecules (self-scavenging). This argument was used in the past to exclude the presence of caged radical–radical recombination. More recently, however, the efficiency of this self-scavenging process has been seriously questioned[37] and it seems possible that the drastic increase in the retention/inversion ratio in the presence of Br_2 is due to highly efficient scavenging of the ^{38}Cl (in the cage) by Br_2. This being the case the experimental results would suggest that the primary ^{38}Cl attack is made almost entirely by a front-side approach.

(37) For a discussion of this question see, e.g., G. Stöcklin in "Hot Atom Chemistry Status Report", IAEA, Vienna, 1975, pp 161–181, and subsequent discussion section, pp 181–190.

The Solvatochromic Comparison Method. 6. The π^* Scale of Solvent Polarities[1]

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Abstract: Seventy solvents are arranged in a π^* scale of solvent polarities, so named because it derives from and best correlates solvatochromic effects on $p \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic spectral transitions. Solvent effects on ν_{max} values of seven primary indicator compounds are employed in the initial construction of the π^* scale, and correlations with 40 additional spectral indicators are used to expand and refine the data base. Standard deviations in the 47 correlation equations of ν_{max} with solvent π^* values average 0.11 kK, which compares well with the 0.10 kK precision limit of the solvatochromic comparison method. A number of stratagems are employed to exclude or minimize hydrogen bonding effects in determining π^* values of HBA (hydrogen bond acceptor) and amphiprotic HBA-D (hydrogen bond acceptor-donor) solvents. Values of s in the solvatochromic equation, $\nu_{max} = \nu_0 + s\pi^*$, show logical variations with indicator structure, lending confidence that this new solvatochromic parameter will come to serve as a convenient and meaningful indicator of the interaction of a chromophore with its cybotactic environment. Poor correlation of ν_{max} values for Dimroth's betaine, 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide with the π^* scale is rationalized in terms of differing polarity and polarizability contributions to overall solvent effects.

In earlier papers of this series,[3-5] information obtained through solvatochromic comparisons was used to construct an α scale of solvent HBD (hydrogen bond donor) acidities and a β scale of solvent HBA (hydrogen bond acceptor) basicities.[6] These were intended to serve, together with an index (or indexes) of solvent polarity-polarizabilities (SPP's), toward rationalization of solvent effects on many free energy related properties through a schematic equation of the form,

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + a\alpha + b\beta + \mathrm{SPPE} \qquad (1)$$

XYZ in eq 1 may represent a reaction rate or equilibrium constant, or a position or intensity of spectral absorption; a and b are measures of the susceptibility of XYZ to changing solvent HBD acidity and HBA basicity, respectively; and SPPE denotes the solvent polarity-polarizability effect. In the present paper we direct our attention to the SPPE term in eq 1.

Koppel and Palm[7] have dealt with the SPPE problem by incorporating separate polarity and polarizability terms in the multiple parameter equation with which they have correlated solvent effects on a variety of XYZ's,

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + yY + pP + eE + bB \qquad (2)$$

The E and B terms in eq 2 represent solvent electrophilicity and nucleophilicity (and correspond in intent to our α and β in eq 1);[8] the Y term represents one or the other of the solvent "polarity functions", $(\epsilon - 1)/(\epsilon + 2)$ or $(\epsilon - 1)/(2\epsilon + 1)$; and the P term corresponds to the "polarizability function", $(n^2 - 1)/(n^2 + 2)$. Equation 2 has had fair to excellent success in correlating large numbers of solvent dependent properties.

In this work we have used solvatochromic comparisons of UV-visible spectral data to assemble a π^* scale which evidently combines polarity and polarizability in such a manner as to give an index of single-valued SPP parameters. This π^* scale is so named because it derives from and best correlates solvatochromic effects on $p \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic spectral transitions. However, certain applications of the π^* scale to other types of solvent effects will also be shown. When the π^* parameters are used to quantify SPP effects in eq 1, the equation becomes,

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + s\pi^* + a\alpha + b\beta \qquad (3)$$

with s representing the susceptibility of XYZ to changing SPP.

We prefer this alternative, *seemingly* more empirical approach to that of Koppel and Palm for a number of reasons: (a) One fewer parameter in eq 3 compared with eq 2 allows significant simplification of the correlations and easier testing of their statistical validity. (b) The $(n^2 - 1)/(n^2 + 2)$ and $(\epsilon - 1)/(2\epsilon + 1)$ terms are interrelated ground state properties of the bulk solvent, whereas we are more concerned with effects at the molecular level which occur in solute-organized cybotactic regions (i.e., within the solvation shells)[9,10] and derive from excited or transition state dipole-dipole and dipole-induced dipole interactions. (c) Fowler, Katritzky, and Rutherford,[11] in their extensive and well-reasoned parametric analysis of solvent effect correlations, found no combination of functions of ϵ and n with other parameters which adequately correlated more than a small proportion of the XYZ's considered.

In assembling the π^* scale, we were alerted by the admonitions of other researchers in the field to avoid certain of the pitfalls encountered by earlier workers who had reported solvent polarity scales on the basis of the solvatochromic behavior of indicator solutes. In this vein, for example, Figueras[12] had presented convincing evidence that "solvent polarity scales based on shifts in λ_{max} of an indicator dye are of limited value