~~Appendix IV~~

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Caging in High Energy Reactions

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Despite frequent discussions of the "cage effect" in hot atom reactions originally postulated by Willard in the early days of hot atom chemistry and subsequently investigated by several authors, its exact role in actual systems remains in most cases still highly speculative.

The idea of caging goes back to Franck and Rabinowitsch who first proposed that a diffusion - limiting solvent cage could increase the efficiency of photochemically initiated radical combination under condensed phase conditions. In the further development of this concept Noyes suggested to make a distinction between primary cage effects, where the photofragments remain almost within bonding distance of another until they lose enough energy to recombine, and the secondary effect which is diffusive in nature, where the fragments initially seperate to some distance but later find each other again. The secondary effect can usually be suppressed by the presence of scavengers.

In the case of typical hot atom reactions, e.g. in hot substitution processes several types of cage effects can be postulated. According to the reaction scheme shown on fig. 1, the hot atom x will collide with the molecule and form a "sticky collision" complex, which in the condensed phase could be stabilized by frequent collisions with the

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surrounding molecules to a "caged complex", as postulated by Stöcklin.

If the result of the collision is the replacement of the atom X by Y forming an excited intermediate then this intermediate has two alternatives. It could become collisionally stabilized, the overall result of this route being an one-step displacement mechanism, or it can decompose before it can stabilize itself. In the latter case decomposition may lead to elimination products and others, or to fragmentation into an organic radical R and Y, which if their recoil energy obtained in the fragmentation process is relatively small can become trapped in the surrounding solvent cage and may eventually recombine.

If the initial collision does not result in the formation of an excited molecule but causes immediate fragmentation to R, X and Y, again the possibility exists that all three species become trapped in the solvent cage and recombination between R and X or Y may occur.

Although schematically caging appears to be a distinct possibility in hot reactions, the basic question which we will have to ask is what concrete evidence do we have for caging in hot atom reactions.

The most widely used argument in favor of the caging mechanism is based on the results of the density variation method first described by Richardson and Wolfgang. These authors observed substantial $CH_3{}^{18}F$ and $CH_2F^{18}F$ radiochemical yield enhancement as the result of ^{18}F for F or H substitution in CH_3F when they increased the density of the system, which was ascribed to Franck-Rabinowitsch caging (fig. 2).

Other evidence which seemed to be consistent with a caging mechanism was the drastic increase observed in the yields of inverted product in the ^{38}Cl for Cl substitution in diastereomeric molecules such as 2,3-dichlorobutane in the gas to liquid phase transition (fig. 3).

Now let us consider these pieces of evidence in greater detail. First the Richardson-Wolfgang density plots.

By ascribing the second increase in product yield at higher density to caging they had to exclude further deexcitation - stabilization of supposedly highly excited species formed in the primary step (fig. 4). Richardson and Wolfgang did that by using a rather intuitive lifetime argument, in which they postulated that at these high densities a large fraction of product molecules would have to be stabilized before they have moven more than a few tenth of an Å. This would imply lifetimes of the order of a vibrational period or less, meaning that the entity was not bound in the first place.

Only if one accepts this reasoning namely that no further deexcitationstabilization occurs at these densities can the onset of the further increase in the product yield be identified with the begin of caging reactions. While this Richardson-Wolfgang explanation was accepted for some time in the absence of any dissenting evidence, it was recently seriously questioned by Root et al., Welch et al., Stöcklin et al., and Rack et al.

Root and coworker studied the ^{18}F for F substitution of CF_3CH_3 where they found a qualitative similar yield-density variation dependence as Richardson and Wolfgang for the same process in CH_3F (fig. 5). Root et al. preferred to replace the conventional bulk

density correlation by a comparison of the variation of experimental yields with the to called reduced length parameter, λ/σ, which represents the ratio of the mean intermolecular seperation distance to the molecular diameter of the host substance:

$$\lambda = \{6M/\pi pL\}^{1/3} \times 10^{8}\ \text{Å} \quad \text{(close packed sphere model)}$$

(M = molecular weight; P = density, L = Avogadro's number)

A plot of the absolute hot yield as a function of λ/σ, which is in this case basically a function of the reciprocal of the density is shown on the graph (fig. 6). The authors define as the apparent $CF_2{}^{18}FCH_3$ yield, the actually observed relative $CF_2{}^{18}FCH_3$ yield and also determine what they call the mechanism yield, which includes all the products which the authors postulate to result from ^{18}F for F substitution.

While the apparent yield increase at lower λ/σ ratios could possibly be explained by a concurrent increase in the deescitation-stabilization process, no such explanation appears likely for the increase of the total mechanism yield. Furthermore while the apparent yield monotonically increases over the range from 2.0 to 5.0, a plateau is formed in this range for the mechanism yield, which drastically and abruptly increases at about 2.0. From these findings Root et al. conclude that the observation of an intermediate density plateau for one particular product on a Richardson-Wolfgang plot does not constitute conclusive evidence for the onset of caging reaction unless a total mechanism study has been performed, or unless the role of deexcitation stabilization has been quantitavely established on experimental grounds apparent product yield enhancements observed at large densities cannot be attributed solely to caging. These

authors subsequently suggest a quantitative determination of caging yields in hot atom systems. As a result of this rather involved treatment based on a complete mechanism analysis they arrive at the caging yields as shown in table 1.

While this investigation seems to have established the existence of caging in hot atom reactions, at least in the case of the ^{18}F for F in CH_3CF_3, the detailed nature of the caging mechanism is still not unambiguously known.

Machulla and Stöcklin reported on the results of a series of experiments on the pressure and phase dependence of the stereochemical course in hot tritium for hydrogen and chlorine-38 for chlorine substitution in meso and rac. 1,2-dichloro, -1,2-difluoroethane. The results are shown on the graph (fig. 7). The density dependence of the ^{38}Cl for Cl substitution yields resembles the trend observed by Richardson and Wolfgang in $^{18}F/CH_3F$ system as previously discussed and the gas to liquid transition resulting in a loss of stereospecificity of the reaction may be explained by radical caging, which would affect the chlorine but not so much the much smaller T atoms. There are however certain features which are difficult to reconcile with the radical - radical cage recombination mechanism. The first argument against the presence of caging in this system is according to the authors that hydrogen abstraction by (thermal) chlorine atoms formed as of the primary substitution process from the molecules which form the solvent cage would be a fast reaction which should compete strongly with radical recombination. Furthermore the authors argue that if the enhancement of the ^{38}Cl for Cl substitution yield accompanying the gas to liquid phase change would

be due to cage recombination between ^{38}Cl and the organic radical, both diastereomeric product yields would increase, depending on the thermodynamical or kinetic control of racemization and recombination respectively. The fact that in both diasteromers an identical phase effect is observed therefore does not provide any evidence for a radical recombination.

Additional information is derived from the pressure dependence of the yields of elimination products. While in the case of T for H substitution the yield of elimination products decreases as expected with higher density and eventually levels off the opposite trend is observed which doesn't agree, again according to the authors with a deexcitation - stabilization mechanism, where unimolecular decomposition should cease at higher pressures.

The authors therefore suggest a new mechanism which involves a "caged complex". They argue that at higher densities particularly in the liquid phase the collision times are longer, the tightly packed molecules are kept together and the time of interaction is prolonged. In addition they reason that solvation and efficient energy transfer may promote hot radical-molecule interactions, which cannot occur in isolated gas-phase collisions. They visualize the caged complex as an adduct formed from the hot atom and substrate molecule, which has a lifetime long enough to allow e.g. racemization or substitution by inversion of configuration.

This idea of a caged comples was followed up by Rack and his coworkers. By studying n,γ activated reactions of ^{128}I with acetylene they found it convenient to explain their observed results in terms of an excited complex formed by the attack or addition of the I^+ ions to the triple bond of the acetylene molecule (fig. 8). They also

expand on the nature of this caged complex and comment that while it would be desirable to characterize the nature and lifetime of reaction complexes on a rigid mathematical basis employing the arguments presented by Richardson and Wolfgang it is virtually impossible for the following reasons:

(1) the distribution of the atom's translational energy into internal and translational modes of the comples is not known;

(2) the intermolecular distance required in the collisional lifetime calculations is dependent on the microscopic density which cannot be assumed identical with the macroscopic density because of local perturbations and possible radical formation;

(3) the unimolecular rate constants for RRKM kinetic lifetimes is experimentally unobtainable; and

(4) the energy distribution function is non-Boltzmann in nature as a result of incomplete thermalization.

A "true" unimolecular complex requires $\geq 10^{-12}$s to completely randomize internal energy. Lifetimes of this magnitude require low internal energies and small collision numbers. These conditions require thermal or near-thermal systems at low to moderate pressures. An order of magnitude calculation of the collisional lifetime in comparison with simple RRK kinetic lifetimes indicates that the condensed phase iodine-acetylene reaction complex is collisionally limited and of the order of a vibrational period or less ($\sim 10^{-14}$s). One must conclude that an insufficient time is available to the complex for energy redistribution and concede the possibility that the complex might not be chemically bound as a result of lack of vibratkonal modes. Although gas phase calculations appear to be of the

same order of magnitude (10^{-13} to 10^{-12}s) or greater than RRK calculations, the lifetime cannot be ascribed to collisional or kinetic limitation because of large uncertainities in the calculations. In either case, it is only possible to obtain sufficient time for energy redistribution at low pressures and low internal energies.

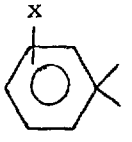
The caged complex has several features which are especially attractive to the experimental organic or physical organic chemist, since in this case principles of the classical organic chemistry can be applied to explain certain substitution mechanisms, and the effect of chemical factors such binding energy, electronegativity and electron density produced formation can be rationalized.

This has been recently demonstrated by Stöcklin et al. in the pronounced selectivity and reactivity which hot chlorine atoms show in substitution reactions with aromatic systems.

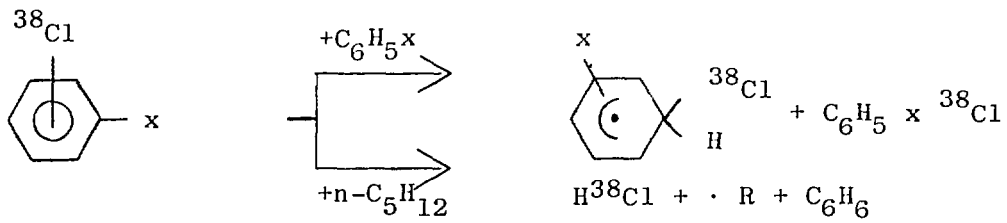
In contrast to the results obtained in aliphatic systems the ^{38}Cl for F and ^{38}Cl for H substitution in fluorobenzene shows only a slight pressure dependence and only the gas to liquid phase transition is accompanied by a significant product yield increase (fig. 9). The same observation is made for the isomerdistribution (table 2). While in the gas phase over the whole range from 10 - 15000 torr the distribution is practically statistically and remains unchanged in the liquid phase a distinct increase in the yield of the para isomer on account of the meta products has been observed which would indicate a directing effect of the F substituent. It should be mentioned that argon moderators had no effect on the isomerdistribution in the gas phase.

In dilution experiments, i.e. by adding pentane to the liquid reaction system the authors were able to discern two different reaction mechanisms. The addition of pentane generally reduces the products from ^{38}Cl for Cl or H substitution in the fluorobenzene - pentane system as shown in the graph not linearly but a concave is obtained (fig. 10). If the results are corrected to zero mole fraction of n-pentane the corrected substitution yields are obtained as shown (fig. 10).

The authors interpret the results of the ^{38}Cl for H substitution in terms of two different channels, a multistep process and a single step process. While the multistep process is eliminated by larger amounts of solvent present the one-step is not affected by the solvent. Such a one-step seems to control also the ^{38}Cl for F substitution. According to the authors the aromatic Cl for H substitution is only a minor process in the gas phase which proceeds with little selectivity. In the liquid phase complex formation (rather than cage radical recombination) leads to higher yields via two process: 1). an one step reaction via formation of a σ complex.

$\{^{38}Cl\}^{+} + C_6H_5X \rightarrow$  $\rightarrow C_6H_5{}^{38}Cl$

and 2). a two or multistep reaction involving first the formation of a Π complex, which subsequently can undergo rearrangement to form a σ complex or react if pentane is present by hydrogen abstraction:



A typical feature of this latter process would be a higher selectivity in the isomer distribution which is borne out in table 3, where the relative isomer distributions have been seperated in the contribution made by the two processes. There is other evidence supporting this hypothesis, e.g. the observed linear free energy relationship as shown in the Hammett plots which indicate the elctrophilic character of the substituting chlorine recoil atom.

In summary the authors rationalize the substitution in terms of a primary high energy step leading to the non rate determining formation of a complex while the final product formation and positional selectivity seems to be essentially a thermal process.

Although some of the results mentioned could possibly also explained by a caged radical mechanism the fact that the yields of T for H substitution in aromatic substrates exceeds that of Cl for H would be inconsistent with the widely assumed picture that atoms cannot be sufficiently caged but will escape from the solvent cage.

Most of the density variation work so far has indicated that the gas to liquid phase transition has a much more significant effect on product formation and product distribution than a pressure change even if this change covers a wide pressure change, a fact which led to the postulation of the caged complex. It appears therefore that in the condensed phase collision times, solvation and energy transfer

etc. are of great importance.

In a somewhat different context the late Professor Bunker made several computer simulations on the cage efficiency associated with photolysis of a diatom I_2, in a solvent of spherically symmetric molecules CCl_4. On the basis of a classical trajectory analysis with Monte Carlo event selection he came to the conclusion that the recombination is highest when recoil energy is low, solvent molecules are large, and intermolecular attractions appreciable. They reject the previous treatment of the solvent as a continuum and thus the importance of macroscopic parameters, such as viscosity for primary caging and prefer a molecular description of the caging process. While solvent mass appears to be of less importance, caging efficiency increases with a decreasing recoil energy and an increase of mass density or molecule size. The least definitive results were obtained on the effect of intermolecular interactions.

The importance of this study, while certainly incomplete, and thus allowing no final conclusions as to the importance of the various parameters lies in the fact that it directs the attention to the molecular picture of the caging process.

In view of these latter predictions it seems interesting to analyze the effects of solvents in high energy chemistry, especially on product yields and the course of the reactions.

Due to the difficulties involved in the absolute radiochemical yield determination in the presence of solvent the study of the stereochemical course proved to be a convenient tool to investigate these effects. The first experiments in this direction by Wai and Rowland with the diasteromers of 2.3-dichlorobutane neat and in the

presence of relatively large amounts of butadiene seemed to indicate an increase in the retention of configuration of the ^{38}Cl for Cl substitution, which the authors explained in terms of a elimination of radical reactions.

A more comprehensive study was carried out by Vascaros, Machulla and Stöcklin who studied the stereochemistry of the ^{38}Cl for Cl in the same compounds. They related the observed solvent dependence to the relative abundance of the conformational isomers which vary as a function of nature and concentration, and thus in turn to the relative probability for front or back side attack in the various conformers, leading to substitution via retention or inversion of configuration respectively (fig. 11). Such a conformational effect would indeed be evidence for an one step substitution mechanism.

The effect of the solvent on the stereochemistry of the ^{38}Cl for Cl substitution had, however, to be reinterpreted when experiments in our own laboratory showed that even in those cases where a change of concentration or nature of solvent does not induce a corresponding change in the relative conformer abundance, a distinct solvent effect can be observed, as in the case of 2,4-dichloropentane, where only one major conformer is present, whose concentration is only negligibly affected by the nature or concentration of the solvent (fig. 12 and 13). Similar effects have been observed in the case of dichlorohexafluorocyclobutane, where although only one isomer is present, the stereochemical course of the reaction changes drastically in the presence of various solvents (table 3).

Thus other parameters had to be held responsible for the occurence of the solvent effect. By measuring the retention to inversion ratios

for about 30 different solvents and trying to find a correlation between these values and the physical properties of the solvent such as density, polarizability, surface tension, viscosity molecular diameters, and others, we came to the conclusion that the best fit is obtained between the retention to inversion and the dielectric constant or more precisely the term $(\varepsilon-1)/(2\varepsilon+1)$ (fig. 14 and 15). The physical meaning of this correlation can be recognized if one considers the fact that the free energy change involved in the transfer of the solute molecule from the gas phase to the solution: AF is given by the Kirkwood equation, which contains two terms, the cavity term and the interaction term, the latter containing the factor $(\varepsilon-1)/(2\varepsilon+1)$.

Thus the observed correlation may reflect the dependence of the retention/inversion ratio on the solute - solvent interaction in the solution.

What does this correlation tell us about the mechanism of the substitution, or how can it be rationalized in terms of the existing models?

If we consider first a one step mechanism including two reaction channels, one leading to the retained, the other to the inverted product, each one showing a different deexcitation - stabilization characteristics, then one could postulate that an increased solute - solvent interaction leads to enhanced energy transfer and by making certain assumptions about the energy dependence for front vs back side attack, leading to retained or inverted product respectively, one can rationalize the observed results (fig. 16). The effect of solvent on the deexcitation of an excited species has been well documented by

several authors, e.g. by changes in the absorption spectra, or fluorescence spectra of a variety of probe molecules in the presence of different solvents.

In terms of the radical - radical recombination model the implication would be that strong solvent - solute interaction prevents the intermediate organic radical from obtaining planarity before recombination occurs and thus recombination occurs mainly by forming the product which was obtained in the initial replacement step (fig. 17).

It seems also tempting to treat these results in terms of the caged complex model. In this case, where a concerted action consisting of the motion of the incoming chlorine, the outgoing chlorine and the rest of the molecule must be assumed, one can visualize the effect of the solvent by the tendency of the strongly interacting or polar solvent of pulling away the chlorine which is to be replaced from the neighboring carbon atom thus allowing the chlorine-38 to make the attack from the frontside resulting in retention of configuration, whereas in a more inert medium no such movement occurs and a greater fraction of the substitution process occurs via backside attack (fig. 18). This assumption has its parallel in a variety of classical substitution reactions in ordinary thermal organic chemistry.

A major argument against the radical - radical recombination was the assumption that Cl or F radical would be selfscavenged by the molecules forming the solvent cage, e.g. by hydrogen abstraction, a reaction which requires only very little activation energy and would consequently favorably compete with the recombination process.

Root recently investigated liquid phase fluoroethane/H_2S mixtures

to assess the susceptibility of primary caging to interference by an efficient hydrogen abstraction reaction. The collision efficiency for thermal F → HF in CH_3CF_3 is 0.4 vs 95% in H_2S. These authors measured the relative yields and found that the organic product contributions were not measurably affected by the presence of large concentrations of H_2S. Since according to the authors both caging and unimolecular processes as previously discussed contribute to the formation of organic products the results would indicate that the branching ratios for caging vs. primary hot reactions are insensitive to the H_2S concentration at least up to 50 Mole % or in other words the presence of H_2S does not inhibit caged product yields. The authors suggest that these results support the molecular approach by Prof. Bunker who concluded that once a solvent molecules intervenes, that is, if in this case the F atom undergoes a strong collision with a solvent molecule its recombination with the organic radical becomes highly unlikely, regardless whether the F-solvent collision resulted in hydrogenabstraction and formation of HF, i.e. scavenging or not.

Root and his coworkers feel that of greater importance is the question whether the presence of the solvent resulted in a variation of the energy spectrum of the hot fluorine atoms carrying out the first (F replacement) step leading to differencesin the energy deposited in these excited species and consequently leading to differences in the recoil energy of the fragments when these species break up. The recoil energy should have, as demonstrated by Bunker, a profound effect on the escape probability of the F atom.

In studying the solvent effects on the stereochemical course of the ^{38}Cl for Cl substitution in 2,3-dichlorobutane, 2,4-dichloropentane and 1,2-difluoro 1,2-dichloroethane we consistently found deviation from the correlation between the retention/inversion ratios and the term $(\varepsilon-1)/(2\varepsilon+1)$, most pronounced for bromine, perfluoroheptane and acetonitrile as solvent (fig. 14, 15, 19 and 20). Thus in addition of the effect of intermolecular interactions other factors would have to be considered. In analogy to Roots experiments one might want to explain these anomalies in terms of differences in the recoil energies which the fragments gain when the different excited primary products dissociate. This, however would also imply that retained and inverted products are formed with different amounts of excitation energy.

If we consider on the other hand the effect of solvent size, where one would expect in accordance with Bunkers model, an increase in retention/inversion ratio with decreasing molecular size, no satisfactory relationship can be observed either. Only if one takes into account the mass density a better fit for the bromine results can be observed. It does, however, not explain the anomalities observed for acetonitrile and the very small retention/inversion ration for perfluoroheptane in the 1,2-difluoro 1,2-dichloroethane and hexafluorodichlorocyclobutene systems. It appears tempting to explain these results in terms of "selfscavenging" of the ^{38}Cl by the very reactive Br_2 or by a lack of selfscavenging by the much less reactive perfluoroheptane while the lack of scavenging of the acetonitrile may be understood in terms of a solvent cage oriented in such a way that the more negative CN group forms the inner wall of the cage thus

preventing of the ^{38}Cl from colliding with hydrogen atoms.

Thus in summary, what is the present status of the concept of caging of high energy reaction?

It appears that we still have no easy and unambiguous way, short of a complete and very tedious product and mechanistic analysis, which is feasible only for very few system, to determine the contribution made by caging. One has also to emphasize that some products resulting from the hot reaction with a certain substrate may be formed via caging while others are not.

What have we learned about the mechanism of caging, or cage combination vs caged complex?

We have on one side the results from Roots work of the reactions of hot ^{18}F with the CF_3CH_3 system which seems to provide evidence for caging, with ^{18}F being the caged moiety, thus proceeding via a radical - radical recombination mechanism. Their work with H_2S additive also seems to indicate that scavenging via hydrogen abstraction from H_2S to form does not interfere with the radical - radical recombination consistent with Bunkers molecular approach to explain the cage effects.

On the other side we have a series of observations resulting from stereochemical and combined stereochemical density variation techniques, which seem to favor a caged-complex, while the solvent experiments carried out in our own laboratory would be consistent with either of these mechanisms. It is clear that a more conclusive answer can only be reached by more systematic studies, utilizing the whole range of nuclear reactions such as (n,2n), (n,γ) and E.C. processes in mechanistically well defined systems to elucidate the

effect of variations in the recoil energies, by carrying out studies in different solvents or host substances to assess the effect of the physical parameters, such as molecule size and intermolecular interactions on the escape probability or caging efficiences.

It is my belief that the knowledge obtained in these experiments in not only useful for the understanding of the mechanism of hot atom reactions and it thus not an esoteric plaything for a small number of hot atom chemistry or kineticists but it also has great practical applications for a large number of photochemical processes of industrial importance, where the knowledge of the role of solvents, and the parameters leading to increased cage efficiency, could make a great difference in the photocatalytic product yields.

I don't have to point out that these increase in product yields are of great economical value but that they also might lead to a more effective usage of energy, a factor which we all should be aware of in our research.

Table 1

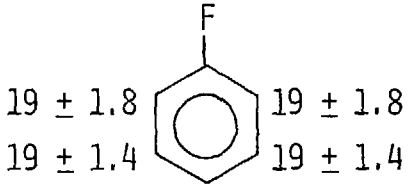
Calculated Caging Yields in Liquid Phase CF_3CH_3 and CHF_2CH_3

Reaction channel	Reactant	Y_c, %	
		303 °K	197 °K
F-for-F	CF_3CH_3	0.7 ± 0.3	2.3 ± 0.4
F-for-F	CHF_2CH_3	1.0 ± 0.3	2.3 ± 0.4
F-for-H	CF_3CH_3	0.1 ± 0.2	1.6 ± 0.5
F-for-βH[a]	CHF_2CH_3	0.6 ± 0.3	1.8 ± 0.4
F-for-αH[a]	CHF_2CH_3	0.8 ± 0.3	1.5 ± 0.3

[a] In CHF_2CH_3 the methyl carbon has been designated β.

Table 2

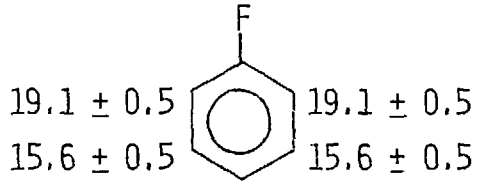
ISOMER DISTRIBUTION FOLLOWING ^{38}Cl FOR H SUBSTITUTION IN FLUOROBENZENE



24 ± 1.6

GAS PHASE

10 - 25,000 TORR
22° - 200° C



31 ± 1.8

LIQUID PHASE

22° C

% Retention of Configuration following ^{38}Cl for Cl Substitution in cis and trans 1,2-Dichlorohexafluorocyclobutane in the presence of Additives (80 Mole %)

Additive	% Retention	
	cis	trans
n-Heptane	88	84
cyclohexane	88	87
n-pentanol	85	85
methanol	--	81
cyclohexanone	82	--
none	76	77
n-perfluoroheptane	55	72

Table 3

CAGING IN HOT ATOM REACTIONS

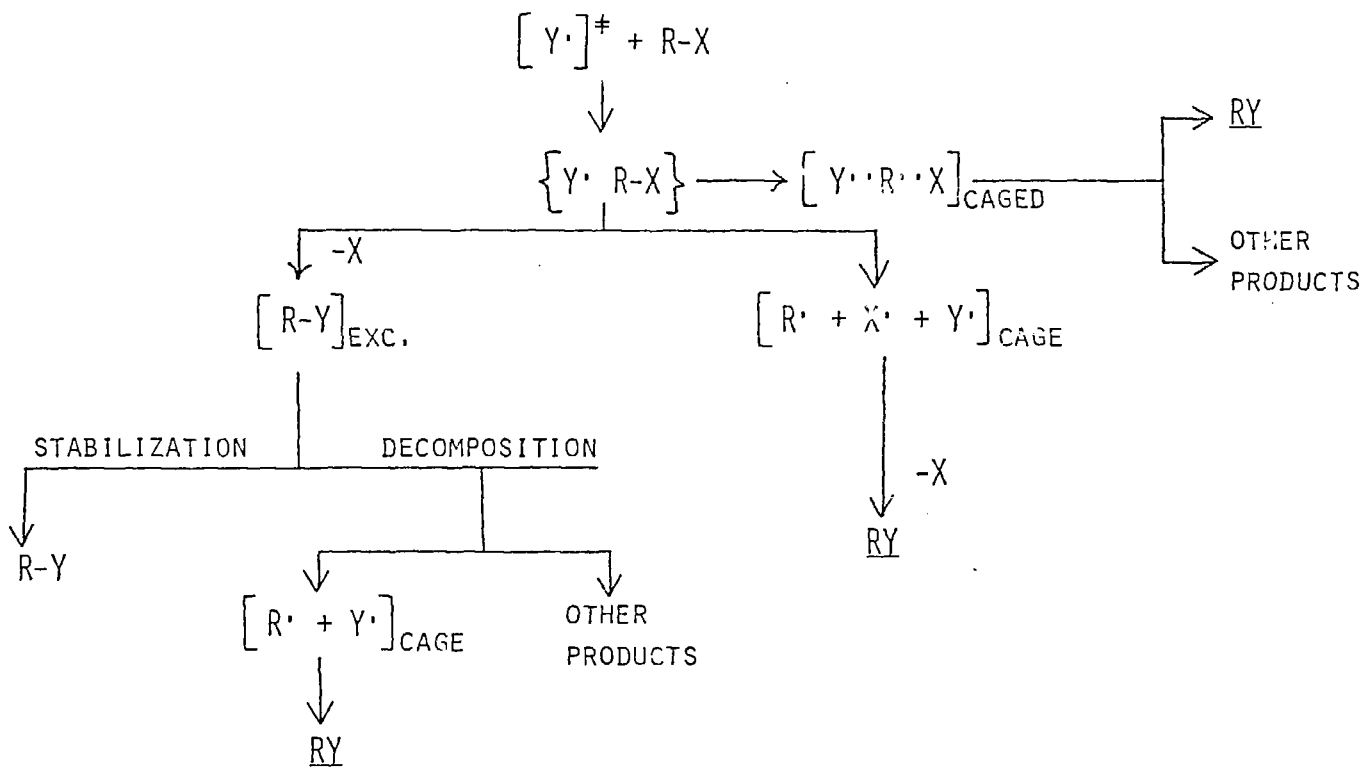
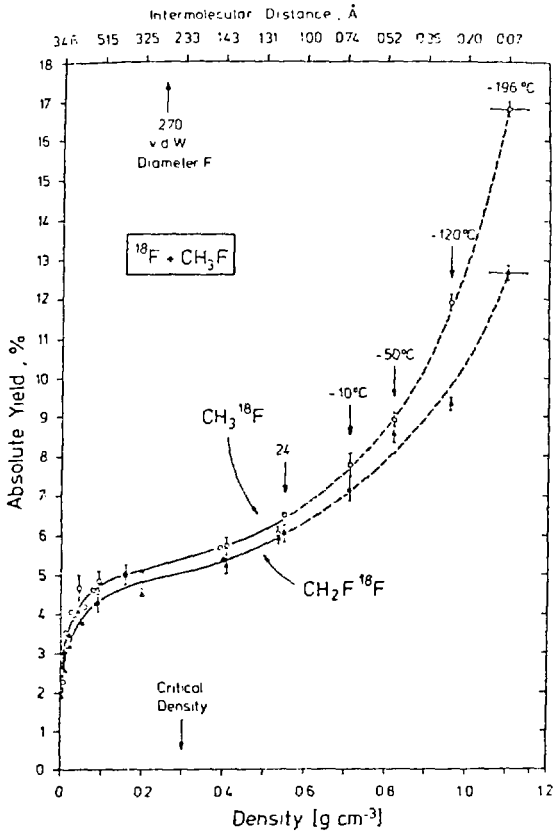


Fig. 1

Fig. 2



[redacted]. Absolute yields of substitution products as a function of density in the CH_3F-I_2 system: C: $CH_3{}^{18}F$, A: $CH_2F{}^{18}F$. Temperature at 55°C unless otherwise specified. Richardson and Wolfgang [14].

Fig. 2

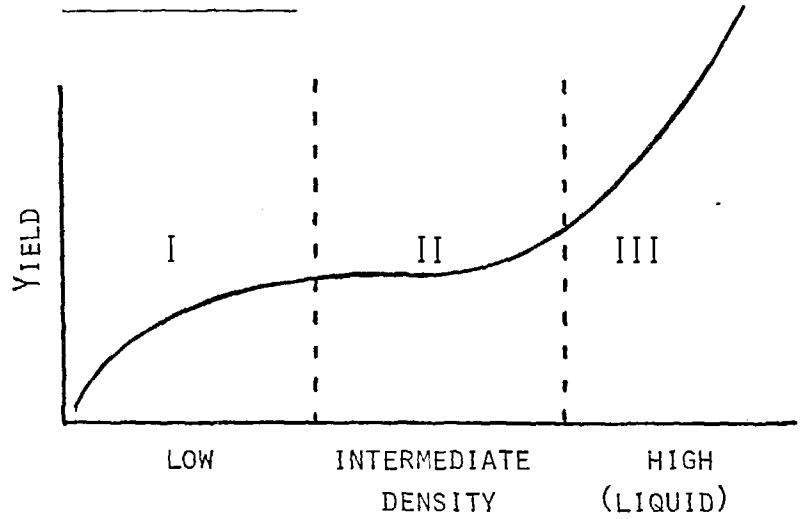
Fig. 3

38 Cl for Cl substitution in
meso or d, l 2,3-dichlorobutane

Substrate	State	Product % meso	Product % d, l
meso	gas	95.0	5.0
	liquid	75.0	25.0
d, l	gas	7.0	93.0
	liquid	25.5	74.5

Fig. 4

DENSITY EFFECT ON SUBSTITUTION PRODUCT YIELD:



I: YIELD INCREASES DUE TO ENHANCED DEEXCITATION-STABILIZATION

II: YIELD LEVELS OFF: ALL EXCITED SPECIES HAVE BEEN STABILIZED

III: YIELD INCREASES FURTHER DUE TO CAGING (OR STABILIZATION OF HIGHLY EXCITED SPECIES; CAGED COMPLEX ETC.)

Fig. 5 and 6

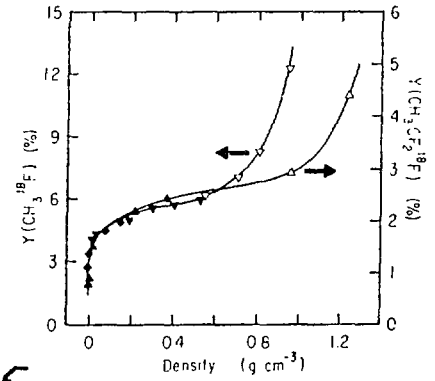


Figure 5. Conventional caging plots for energetic F-for-F substitution in CH_3F and CF_3CH_3: ▼, ▽, CH_3F [redacted]; ▲, △, CF_3CH_3; ♦, plot point overlaps (▼ + ▲); open points represent condensed phase results.

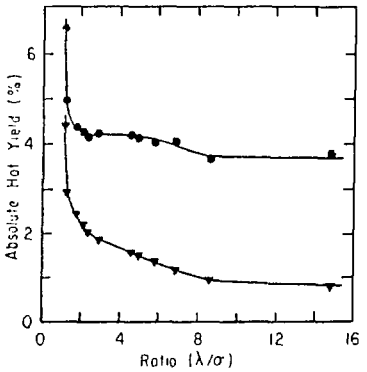


Figure 6. Total mechanism plot for energetic F-for-F substitution in CF_3CH_3: ●, total mechanism yields ([redacted]); ▼, apparent $CF_2{}^{18}FCH_3$ yields.

Fig. 7 and 8

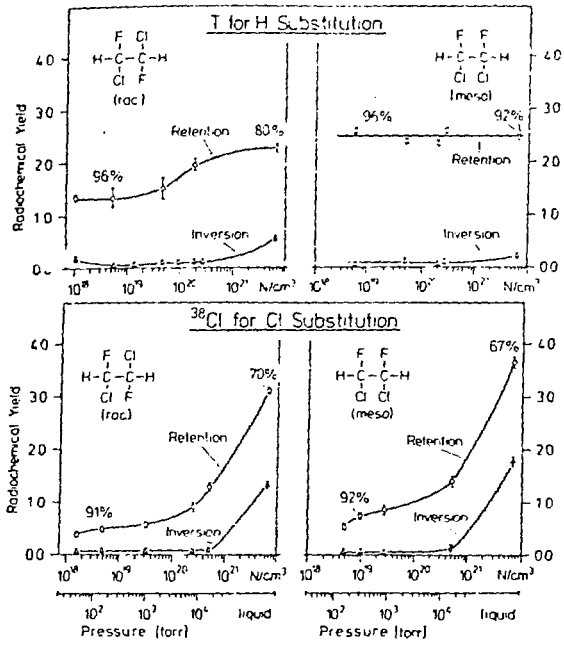


Fig. 7

Scheme I

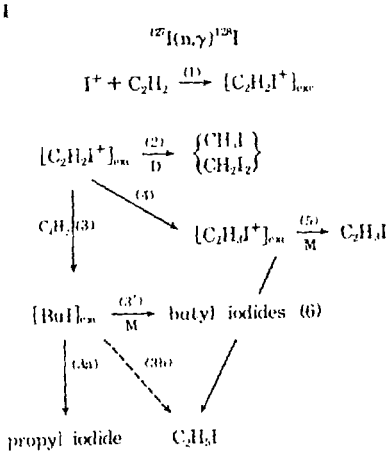


Fig. 8

Fig. 9

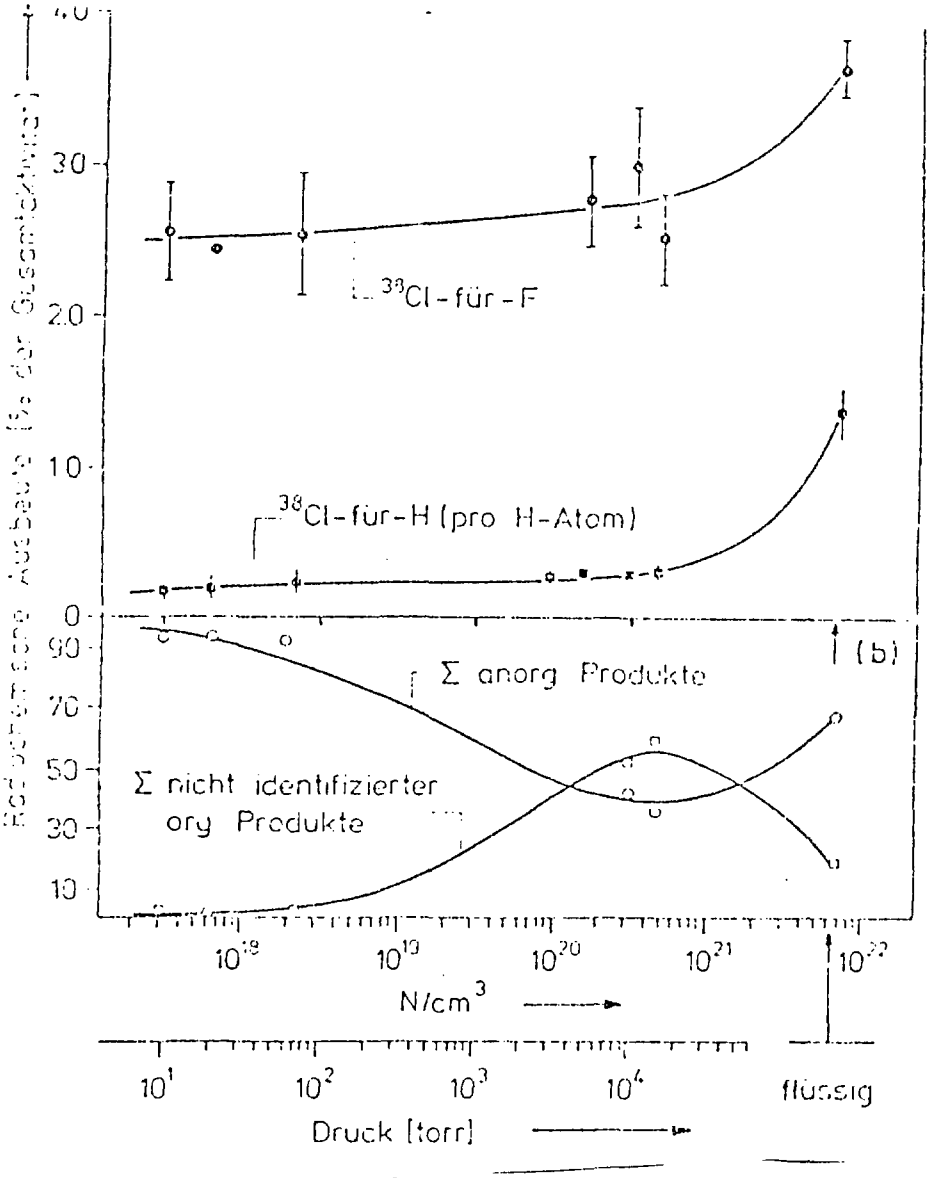

40
30
20
10
0
90
70
50
30
10
^{38}Cl-für-F
^{38}Cl-für-H (pro H-Atom)
(b)
Σ anorg Produkte
Σ nicht identifizierter org Produkte
10^{18}
10^{19}
10^{20}
10^{21}
10^{22}
N/cm^3
10^1
10^2
10^3
10^4
flüssig
Druck [torr]

Fig. 10

Effect of Dilution on H- and F-Substitution by Hot ^{38}Cl-Atoms

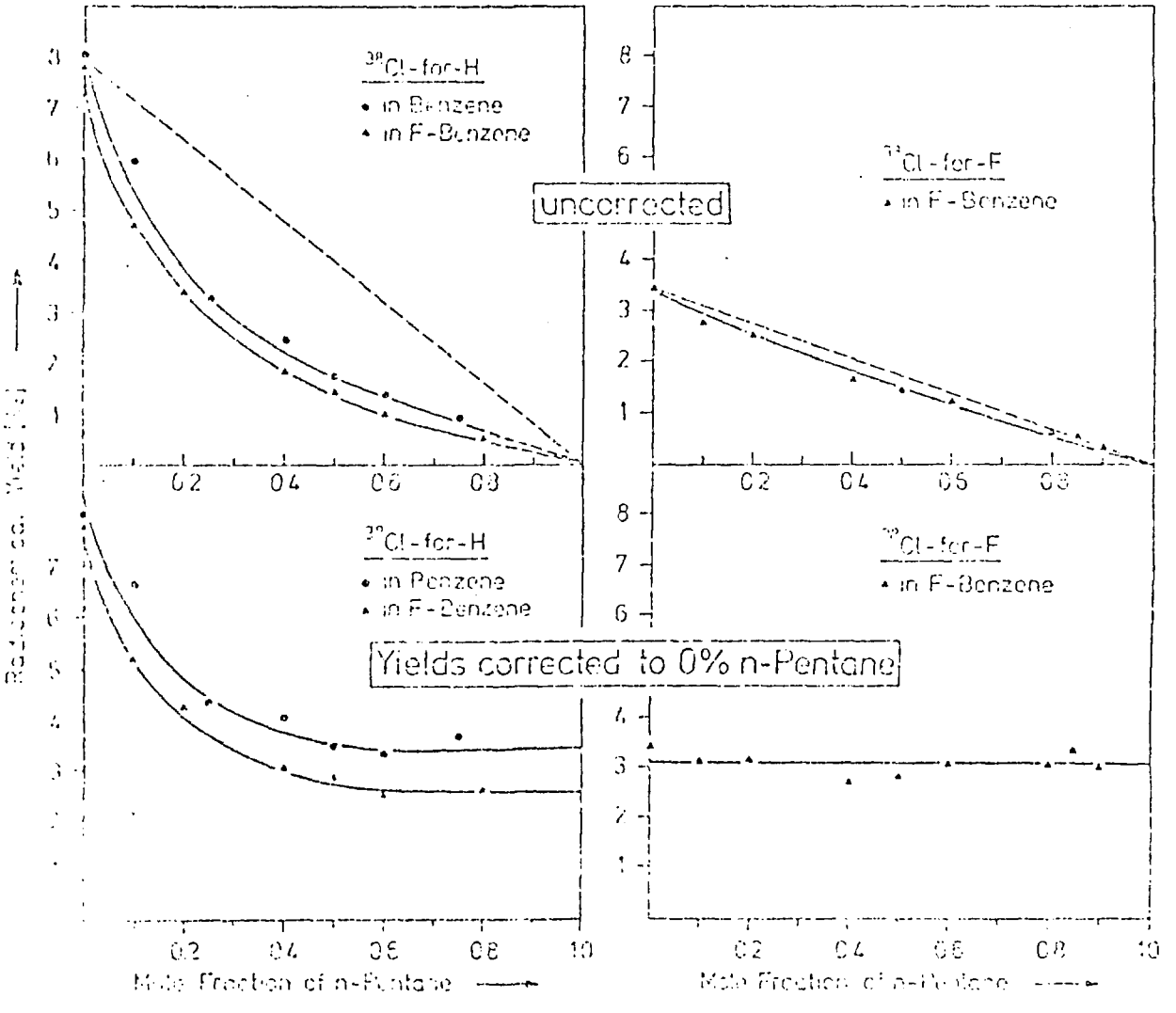
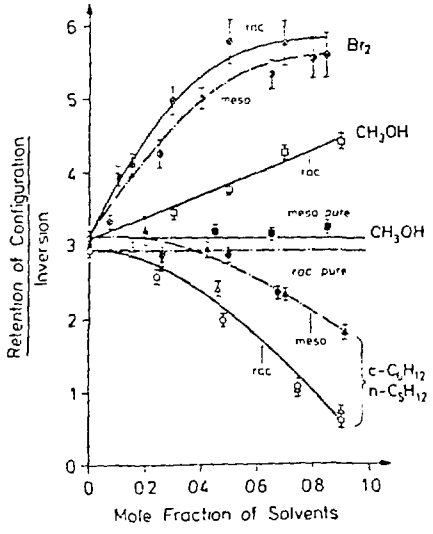
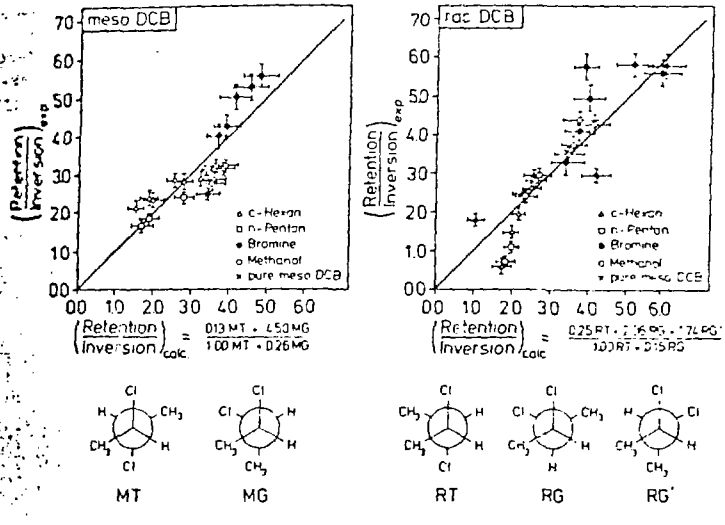


Fig. 11



Solvent effect on the stereochemical course (ratio retention/inversion) of ^{36}Cl-for-Cl substitution in rac- and meso-2,3-DCB.

$$\left(\frac{\text{Retention}}{\text{Inversion}}\right) = \frac{\sigma_{RT}[RT] + \sigma_{RG}[RG] + \sigma_{RG'}[RG']}{\sigma_{RT}[RT] + \sigma_{RG}[RG]}$$



Comparison of computed and measured ratio (retention/inversion) in racemic and meso 2,3-DCB in different solvents. Machulla and Stöcklin [redacted]

Fig. 12

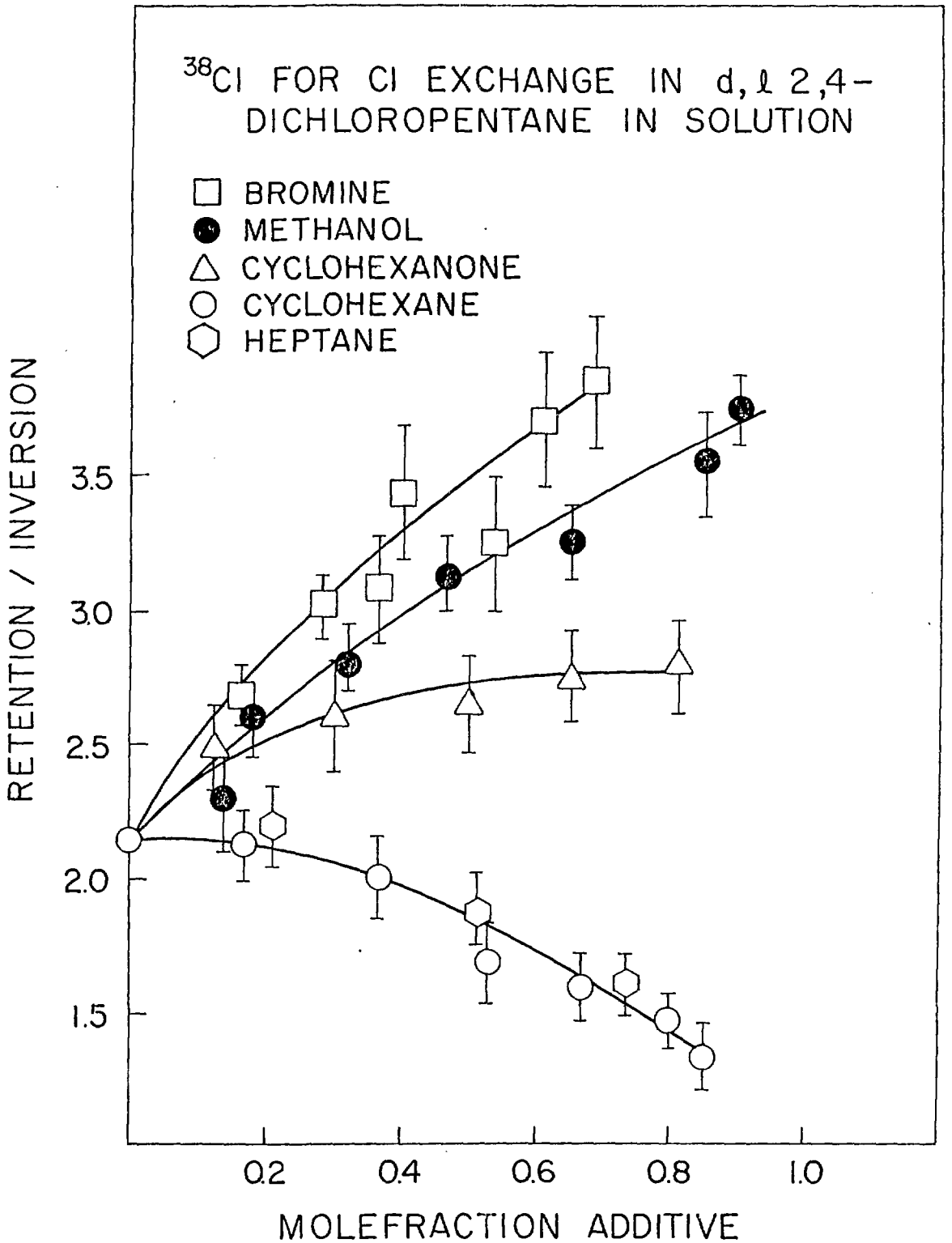

^{38}Cl FOR Cl EXCHANGE IN d,l 2,4-DICHLOROPENTANE IN SOLUTION
BROMINE
METHANOL
CYCLOHEXANONE
CYCLOHEXANE
HEPTANE
RETENTION / INVERSION
3.5
3.0
2.5
2.0
1.5
0.2
0.4
0.6
0.8
1.0
MOLEFRACTION ADDITIVE

Fig. 17

Fig. 13

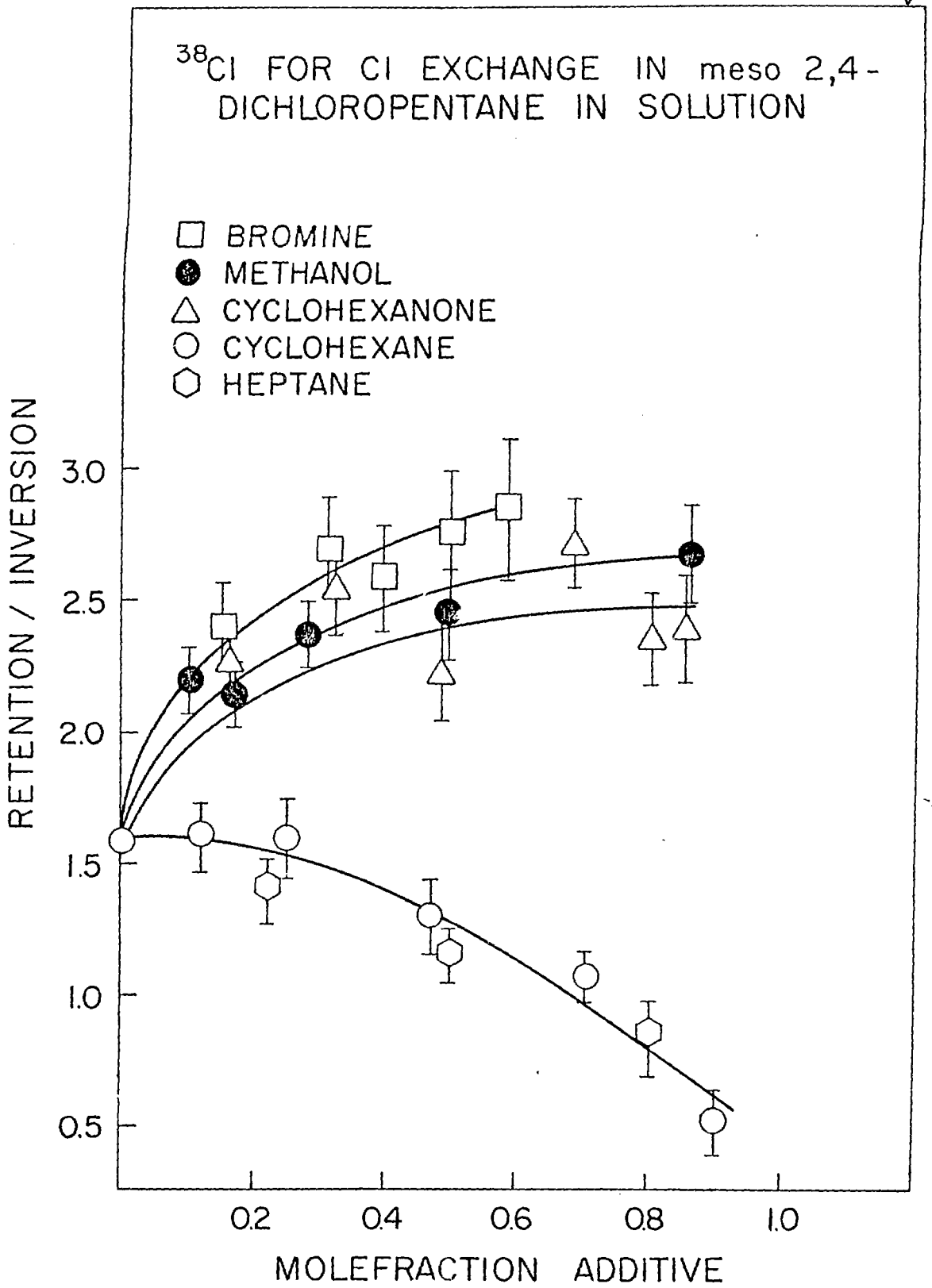

^{38}Cl FOR Cl EXCHANGE IN meso 2,4-DICHLOROPENTANE IN SOLUTION
BROMINE
METHANOL
CYCLOHEXANONE
CYCLOHEXANE
HEPTANE
RETENTION / INVERSION
3.0
2.5
2.0
1.5
1.0
0.5
0.2
0.4
0.6
0.8
1.0
MOLEFRACTION ADDITIVE

Fig. 14

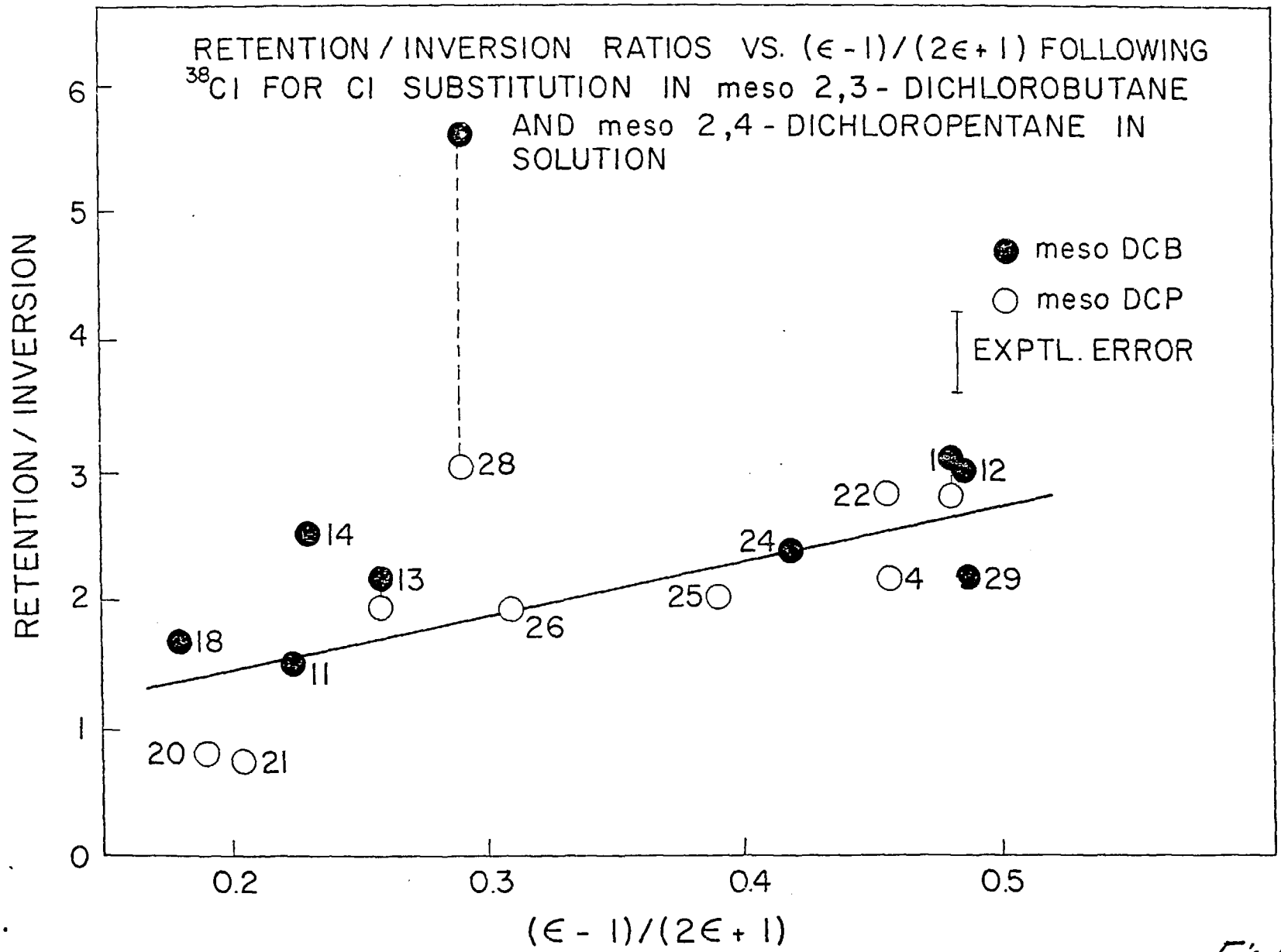

RETENTION / INVERSION RATIOS VS. (ε - 1)/(2ε + 1) FOLLOWING
38Cl FOR Cl SUBSTITUTION IN meso 2,3 - DICHLOROBUTANE
AND meso 2,4 - DICHLOROPENTANE IN
SOLUTION
meso DCB
meso DCP
EXPTL. ERROR
RETENTION / INVERSION
(ε - 1)/(2ε + 1)
0
1
2
3
4
5
6
0.2
0.3
0.4
0.5
28
14
13
18
11
20
21
26
25
24
22
1
12
4
29

Fig 14

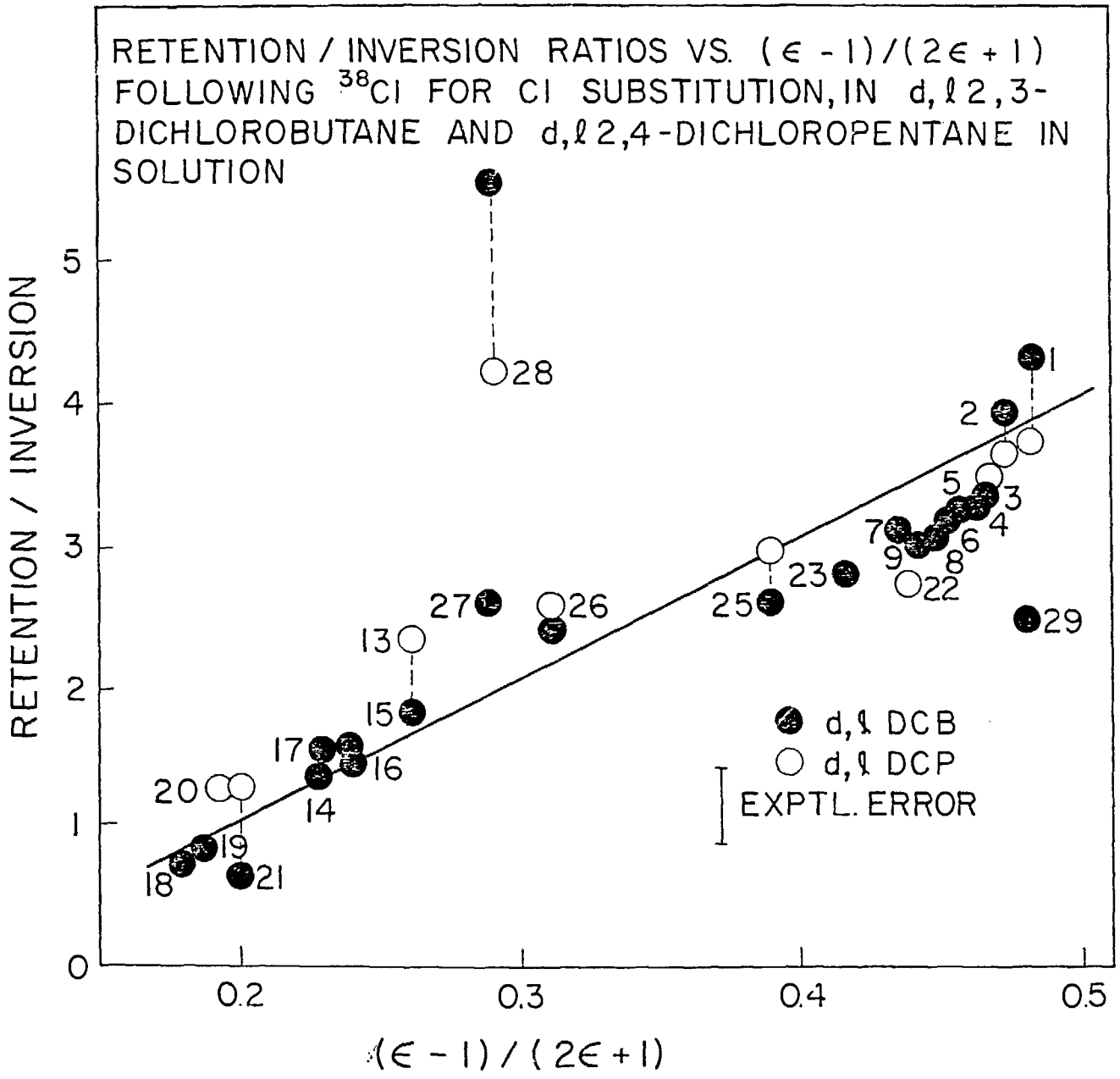
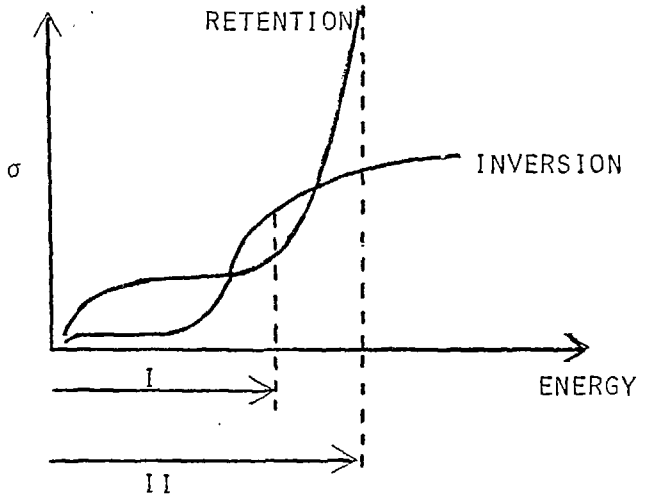

RETENTION / INVERSION RATIOS VS. (ε - 1)/(2ε + 1)
FOLLOWING ^{38}Cl FOR Cl SUBSTITUTION, IN d,ℓ 2,3-DICHLOROBUTANE AND d,ℓ 2,4-DICHLOROPENTANE IN SOLUTION
RETENTION / INVERSION
(ε - 1) / (2ε + 1)
0
1
2
3
4
5
0.2
0.3
0.4
0.5
d,ℓ DCB
d,ℓ DCP
EXPTL. ERROR
1
2
3
4
5
6
7
8
9
13
14
15
16
17
18
19
20
21
22
23
25
26
27
28
29

Fig. 15

Fig. 15

ONE STEP MECHANISM

ASSUMED SUBSTITUTION CROSS SECTION - ENERGY DEPENDENCE: (SCHEMATICALLY)



I PRODUCTS STABILIZED IN WEAKLY INTERACTING SOLVENT,
E.G. PENTANE R/I < 1

II PRODUCTS STABILIZED IN STRONGLY INTERACTING SOLVENT,
E.G. ALCOHOLS R/I >> 1

Fig. 16

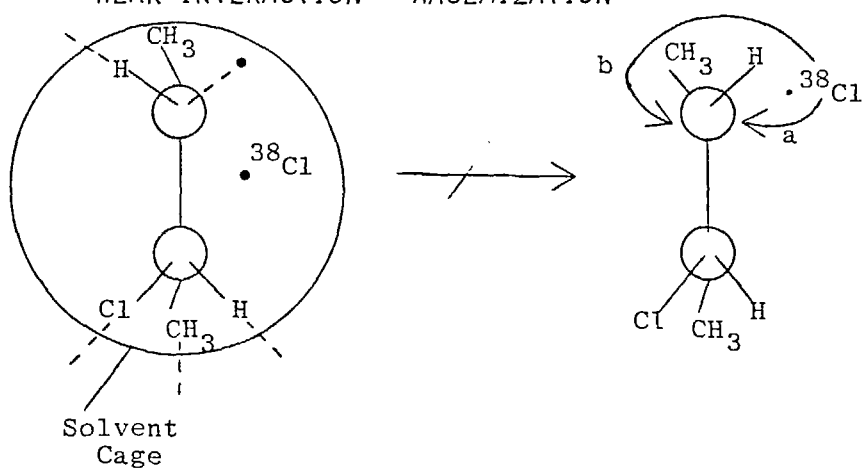
Fig. 17

CAGED RADICAL-RADICAL RECOMBINATION MECHANISM

STRONG INTERACTION BETWEEN RADICAL AND SOLVENT MOLECULES FORMING THE CAGE PREVENTS THE RADICAL FROM OBTAINING PLANARITY BEFORE RECOMBINATION OCCURS:

≡ RETENTION OF CONFIGURATION

WEAK INTERACTION ≡ RACEMIZATION



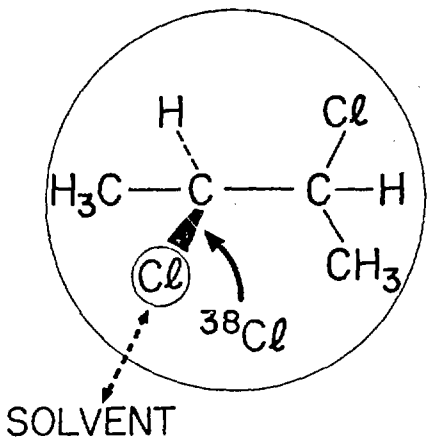
a = RETENTION

b = INVERSION

Fig. 18

SOLVENT–SOLUTE INTERACTIONS DIRECTING STEREOCHEMICAL COURSE (CAGED COMPLEX MODEL)

(a) STRONG INTERACTION



(b) WEAK INTERACTION

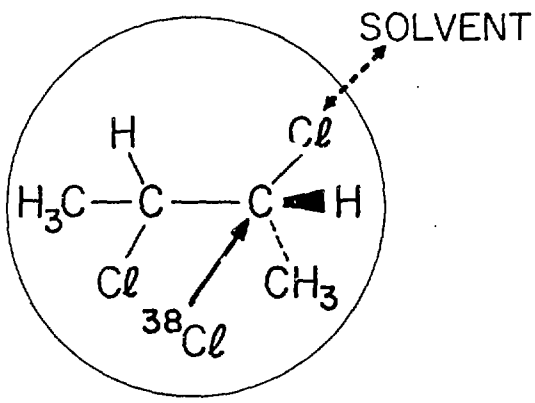


Fig. 19

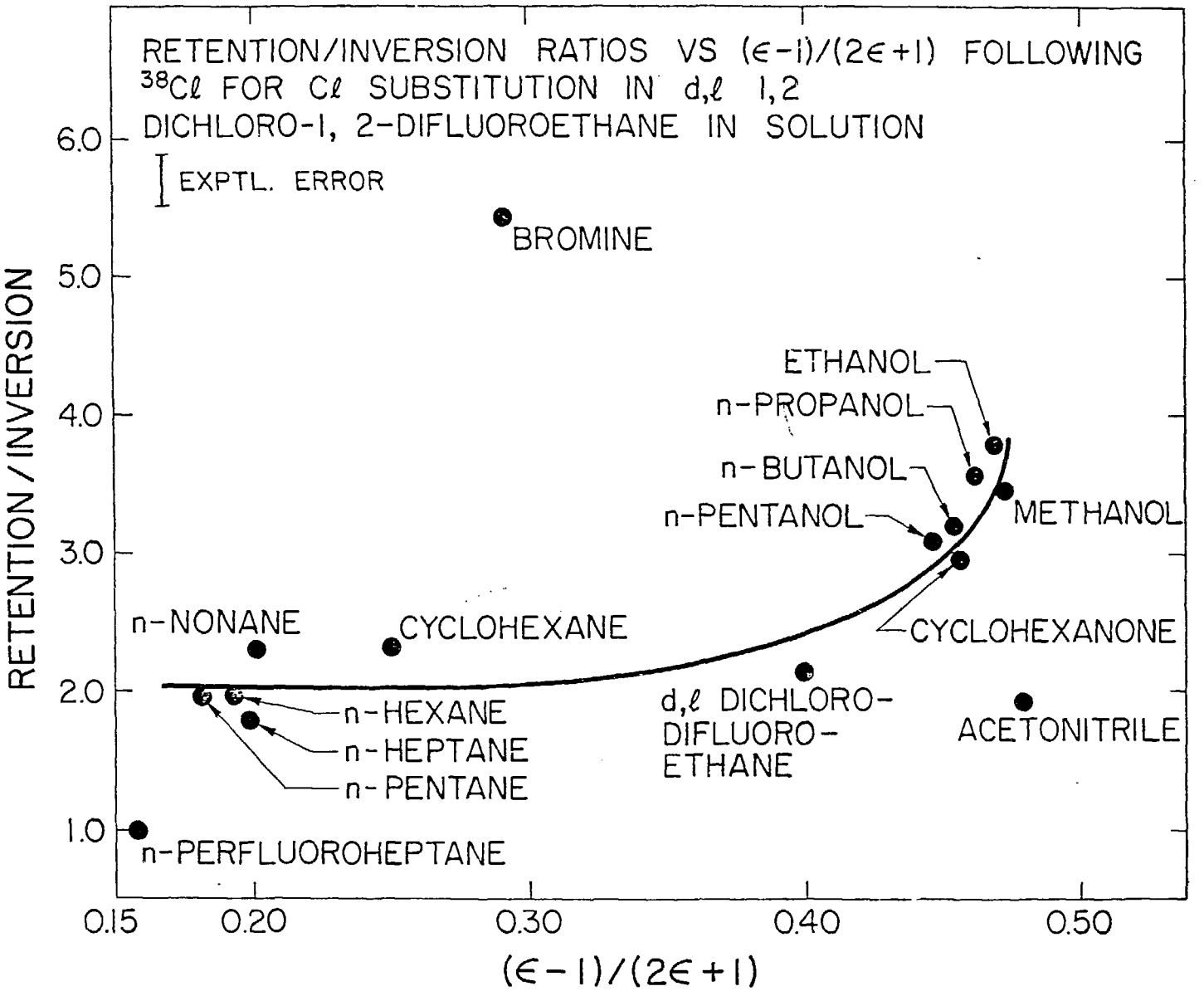
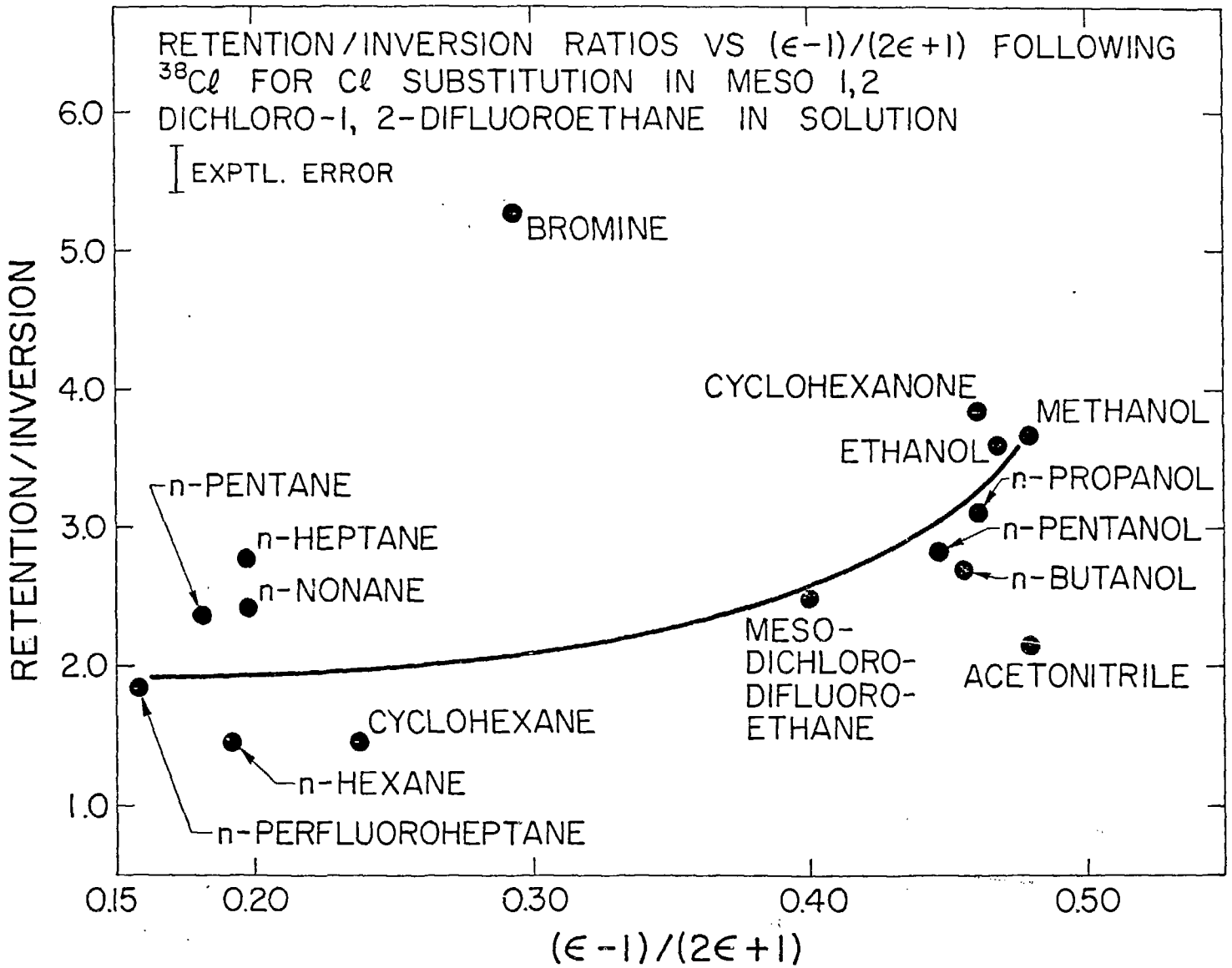

RETENTION/INVERSION RATIOS VS (ε-1)/(2ε+1) FOLLOWING
38Cℓ FOR Cℓ SUBSTITUTION IN d,ℓ 1,2
DICHLORO-1, 2-DIFLUOROETHANE IN SOLUTION
EXPTL. ERROR
BROMINE
ETHANOL
n-PROPANOL
n-BUTANOL
n-PENTANOL
METHANOL
CYCLOHEXANONE
n-NONANE
CYCLOHEXANE
n-HEXANE
n-HEPTANE
n-PENTANE
d,ℓ DICHLORO-DIFLUORO-ETHANE
ACETONITRILE
n-PERFLUOROHEPTANE
RETENTION/INVERSION
6.0
5.0
4.0
3.0
2.0
1.0
0.15
0.20
0.30
0.40
0.50
(ε-1)/(2ε+1)

Fig. 20


RETENTION/INVERSION RATIOS VS (ε−1)/(2ε+1) FOLLOWING
38Cl FOR Cl SUBSTITUTION IN MESO 1,2
DICHLORO-1, 2-DIFLUOROETHANE IN SOLUTION
EXPTL. ERROR
BROMINE
CYCLOHEXANONE
METHANOL
ETHANOL
n-PROPANOL
n-PENTANOL
n-BUTANOL
n-PENTANE
n-HEPTANE
n-NONANE
MESO-DICHLORO-DIFLUORO-ETHANE
ACETONITRILE
CYCLOHEXANE
n-HEXANE
n-PERFLUOROHEPTANE
RETENTION/INVERSION
6.0
5.0
4.0
3.0
2.0
1.0
0.15
0.20
0.30
0.40
0.50
(ε−1)/(2ε+1)