

AN INVITED PAPER TO BE DELIVERED AT THE
8th INTERNATIONAL HOT ATOM CHEMISTRY SYMPOSIUM,
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GAS and LIQUID PHASE HOT ATOM CHEMISTRY: MONOVALENT ATOMS(organic)*

by

EDWARD P. RACK
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NEBRASKA
LINCOLN, NEBRASKA 68508
U.S.A.

When we consider the hot atom chemistry of the monovalent atoms, we not only think of tritium, fluorine and chlorine, but also bromine and iodine. In fact, according to Professor Adloff whose bibliographies have been of great assistance to all of us during the last decade the number of reported studies of bromine and iodine ranked second and third to tritium, respectively. We can generally agree that since the early days most of our experimental and theoretical progress has been with gaseous monovalent hot atoms, hydrogen and the halogens.

In hot atom chemistry - or if we prefer, high energy chemistry or "hot" chemistry, we can produce atoms of high kinetic energies by several routes.

First slide please. (Slide 1)

1. Chemical accelerators
 - (a) atom-molecule
 - (b) ions-molecule
2. Bulb Techniques
 - (a) photochemical recoil
 - (b) nuclear recoil

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In this review we will only consider the nuclear recoil technique for the production of monovalent hydrogen and halogen hot atoms.

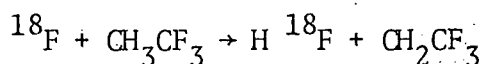
We are familiar with one of the ultimate goals of hot atom chemistry in the description of chemical reactions in terms of excitation functions for each reaction channel. It is obvious to us now that nuclear recoil techniques can not provide us with this specific information. At best, kinetic theories such as that of Wolfgang's and other give an approximate value of the reactivity integral, that is the area under the reaction probability curve when plotted on a logarithmic energy scale. These are the well-known Wolfgang "I" values. We have seen the rapid rise in the early sixties and now in my estimation the decline of the broad use of kinetic theories in hot atom chemistry. Regardless its presence was one of the most stimulating influences in our area.

In my estimation kinetic theories will continue to play a role in understanding the gas phase recoil reactions of tritiumⁱ and other monovalent atoms. On the other hand, we should not use them in their present form for treatment of data involving bromine or iodine reactions activated by radiative neutron capture or isomeric transitions since these activations produce atomic and ionic species of too low kinetic energies. Significant progress in kinetic theory refinement is being made at the present time, especially by Dr. Urch and Dr. Malcolm-Lawes.

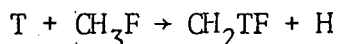
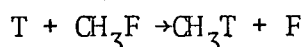
For systems that are amenable to beam studies there is no denying that the depth of information acquired is much greater than from nuclear recoil studies, finding excitation functions and angular distributions for single collision events. However, there are various kinds of studies involving monovalent species in the gas and condensed phase which cannot be accomplished or do not lend themselves well to beam studies. Next slide please. (Slides 2-7)

1. Determination of previously unknown reaction modes quickly and relatively inexpensively. If these appear interesting further studies may be continued using chemical accelerators.
2. Determination of reaction mechanisms for a great number of low pressure and high pressure gaseous as well as condensed-phase systems involving

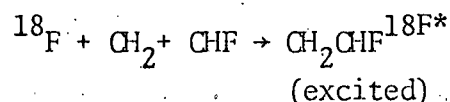
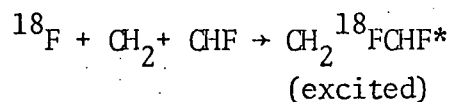
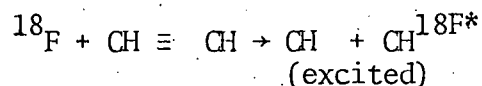
(a) Abstraction



(b) Substitution for another atom (C,H,D,X) or radical (CH₃, etc.)



(c) Addition to unsaturated bonds such as olefins and acetylenes yielding highly excited radicals



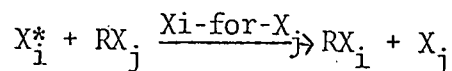
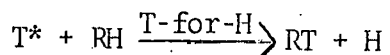
3. Studies involving the gas to condensed phase transition in hot

atom chemistry are not only important in attempting to elucidate the complex condensed state reactions but may provide practical information to materials chemists on the effect of these atoms when formed under irradiation in nuclear reactors.

Up till the present time there have been no definitive views on the nature of halogen hot atom reactions in the condensed state. These difficulties are obvious when we realize the number of points of view employed in the last twelve years as shown in the next slide. (Slide 8)

As shown in the next slide, (Slide 9)

4. Interesting and fruitful studies can involve the stereochemistry of the substitution reactions of tritium and the halogens activated by various nuclear transformations at asymmetric carbon atoms.



The fundamental question of whether high energy monovalent species replace by retention or inversion of configuration at asymmetric carbon atoms can provide insight to the dynamics of hot-atom reactions.

In a thirty minute talk, it is impossible to give a complete review of all the significant work in monovalent organic hot atom chemistry in both the gas and liquid phase. For these omissions I apologize. I will stress recent developments in stereochemistry and the gas to condensed phase transition which are examples of the kind of work I believe are important in putting more understanding to liquid state reactions and to fundamental kinetic knowledge. In the remaining time, if available, I will briefly review recent developments involving the monovalent atoms.

As can be seen on the next two slides, (Slides 10 and 11) various experiments have shown T-for-H substitutions proceed with essentially complete retention of configuration in the solid, liquid and gas phases. Based on experimental results that showed configuration was retained during hydrogen replacement reactions and that showed the effects of steric obstruction to various angles of attack at a given C-H bond, Wolfgang and his co-workers developed the "impact model" (Slide 12) for tritium reactions, which has been somewhat successful in describing gas phase reactions of recoil tritium with alkanes. The impact model suggests a fast, direct displacement ($\sim 10^{-14}$ sec) which is completely independent of bond strengths, but dependent primarily on the point and direction of impact; that is steric restrictions on the trajectory for interactions. Therefore, according to the model, Walden inversion as a displacement event is viewed as unlikely. In order to explain the reactions of hot tritium atoms with halocarbons Wolfgang proposed an "inertial model" (Slide 13) which suggests that substitution is affected by the presence of substituents other than the one being displaced; that is substitution yields are related to the ability of target molecules to rotate rapidly and these "inertial effect" are of a greater magnitude than steric effects in the molecule. As an extension of a general form of the Franck-Condon principle, Wolfgang proposed a "Golden Rule of Hot Atom Chemistry". "Hot atom reactions requiring nuclear motions which are slow relative to the time of collision tend to be forbidden."

In order to explain the systematics of hot fluorine and chlorine reactions with methane and halocarbons, Wolfgang and his co-workers assumed the general features of the "impact" and "inertial" models and proposed a "translational inertial factor" which is more important than the "rotational-vibrational inertial factor" which appeared much less important in halogen than in tritium systems.

As can be seen in the next two slides (14 and 15) previous stereochemical studies of halogen substitution processes have used target models with two vicinal asymmetric centers. The almost complete lack of inversion of configuration of the diastereomers in the gas phase has been used as added support for the application of the impact and inertial models to halogen hot atom reactions. Specifically, the almost complete lack of inversion of configuration of diastereomers in gas systems has been explained as due to reaction collisions short in duration with respect to the time required for movement of carbon atom substituent groups during the inversion process and/or the excited substitution intermediate may undergo unimolecular decomposition during the vibrationally excited inversion process. A lower degree of stereospecificity was observed in condensed-state systems. Whether this is due to a true Walden-inversion or to radical cage reactions leading to racemization of the intermediate was not resolved in these experiments.

In a very important experiment Stöcklin and his co-workers demonstrated the importance of rotational conformation on the stereochemical course of hot halogen for halogen substitution in liquid 2,3-dichlorobutane. The next slide (Slide 16) shows the solvent effect on the retention to inversion ratio for ^{38}Cl for Cl substitution in dl and meso -2,3-dichlorobutane. Briefly what this means is that in the pentane solvent the most predominant conformers are those where inverted attack from the opposite side of the halogen to be replaced can occur.

In order to minimize conformational effects Wolf and his co-workers employed in halogen hot-atom chemistry enantiomers for the first time, 2(S)-chloropropionyl chloride and 2(R)-chloropropionyl chloride, which offer little hindrance to a back-side substitution attack, and the back-side sterically-hindered enantiomer 2(S)-chloro-4-methyl valeryl chloride.

Shown in the next slide (Slide 17) are the absolute yields and percents

retention and inversion of optical configuration of the gas phase Cl-for-Cl substitution at the asymmetric carbon atoms of 2(R)- and 2(S)-chloropropionyl chloride. In the gas phase where mechanistically complicating cage effects are not present, the surprising results of $81^{+8}\%$ and $80^{+2}\%$ inversion of configuration have been observed at the asymmetric carbon atoms for both ^{38}Cl and $^{34\text{m}}\text{Cl}$ substitutions, respectively. The level of inversion has been determined independently for both the R and S isomers of 2-chloropropionyl chloride. This was the first report where net inversion has been observed in any gas phase tritium or halogen hot atom reaction.

The gauche prime conformation of 2-chloropropionyl chloride is significantly more abundant in the gas than in the liquid phase. It is this configuration which provides a relatively unhindered approach to attack of the asymmetric carbon from the back-side as can be seen in the next slides (Slide 18 and 19). In addition, trajectories for chlorine attack leading to Walden inversion may approach within a wide range of angles. Back-side approach to 2-chloropropionyl chloride in gauche conformations is less hindered than for any rotational conformation of $(\text{CHFCl})_2$ or DCB, which are relatively hindered in all conformations. If the open conformation explains why gas phase Cl-for-Cl substitution proceeds with such a high degree of inversion with enantiomeric 2-chloropropionyl chloride, then blocking back-side attack with large substituents should hinder the inversion mode. To test this hypothesis the extent of inversion was measured at the alpha chlorine position of 2(S)-chloro-4-methylvaleryl chloride. The percent retention of $^{34\text{m}}\text{Cl}$ -for-Cl at the asymmetric carbon was found to be $59.3^{+0.3}\%$. This drastic increase in retention compared to 2-chloropropionyl chloride is indicative that the degree of retention (or inversion) is severely affected by steric hindrance.

These results indicated that not all hot-atom substitution reactions are fast and direct involving a front-angle attack but can occur from the opposite side of the molecule involving Walden inversion, in a collision time sufficiently long to allow movements of the substituents.

These results suggest a series of new experiments involving tritium and the various halogens with enantiomeric molecules to further test the generality of the impact and inertial models. Except for tritium reactions with methane where Professor Bunker calculated that the Walden inversion mode is possible, tritium reactions probably occur exclusively by the impact and inertial models. If there is steric obstruction to Walden inversion then reactions may occur with the general features implied by the impact and inertial models. Both direct substitutions (retention of configuration) and substitution involving Walden inversion are possible in hot atom reactions. The relative contribution of both channels may be governed by steric factors.

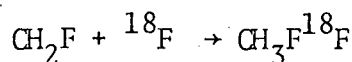
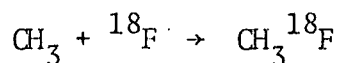
For too many years the hot atom chemistry of gaseous and liquid monovalent atoms was treated as two separate branches of hot atom chemistry. The first important break through relating the two phases has been the Richardson-Wolfgang experiment in 1970.

We all by now are familiar with the Richardson-Wolfgang study involving Fluorine - 19 produced by the $(n, 2n)$ process as shown in the next slide. (Slide 20) Both methyl fluoride and methylene fluoride show sharp rises in yields from the lowest densities leveling off at $\sim 0.2 \text{ g/cm}^3$. This is characteristic of improving collisional deexcitation of primary products formed with such high internal energy that they would otherwise undergo secondary decomposition. A second rise in yields is observed at high densities. These authors felt that it was implausible to ascribe this phenomenon to collisional stabilization of excited molecules.

The most natural explanation of the final rise in yields was that it is due to caging effects.

Hot fluorine atom can break bonds forming radicals such as $\text{CH}_2\text{F}\cdot$ and $\text{CH}_3\cdot$.

The ^{18}F after losing its excess energy can undergo recombination as shown in the next slide. (Slide 21)



In an interesting study, Professor Welch and his groups studied the effects of pressure on the Iodine reactions activated by E.C. and β^+ decay in methane and ethane systems as shown in the next slide. (Slide 22) These systems studies are interesting in that density variations were produced by pressure changes working with gases above their critical temperature. The next slide (Slide 23) is a composite of the Richardson-Wolfgang data on the reaction of ^{18}F with CH_3F as function of the logarithm of the density compared to Professor Welch's data for Iodine-123 reactions in C_2H_6 and $\text{C}_2\text{H}_6/\text{CF}_4$ systems. We can see that the general characteristics of the curves are identical. This similarity helps substantiate the Richardson-Wolfgang idea that the hot reactions of ^{18}F with CH_3F were insensitive to large temperature changes, as the Welch work was obtained in gas phase systems at constant temperatures. Professor Welch suggests that two distant mechanisms are operating at high fugacities. One being a caging reaction involving radicals produced by the activation process and the other involving molecules, whose reactions are governed by the chemical energetics of the hot Iodine-123 species.

As I have been allocated some time later in this session, I will talk about our work involving bromine activated by radiative neutron capture and isomeric transition with halomethanes in the gas to condensed phase transition.

In my estimation one of the most interesting and important studies, one involving stereochemistry and the gas to condensed phase transition is the Machulla and Stöcklin study of hot tritium for hydrogen and chlorine-38 for chlorine substitution in meso and rac-1,2-dichloro-1,2-difluorethane.

We can ask the question how does a continuous increase in density affect the stereochemistry? This is shown in the next slide. (Slide 24) According to Machulla and Stöcklin the density dependence on T-for-H substitution is either very small in the racemic form or negligible in the meso form. The inverted product yield is small over the entire pressure range, increasing only when going to the liquid state. The retained product shows the usual increase in the gas phase generally attributed to increased collisional stabilization of excited products. While the ^{38}Cl -for-Cl substitution yield plot resembles the Richardson-Wolfgang trend, Dr. Stöcklin for various reasons, does not attribute the increase into the liquid state as due to radical caging reactions. Instead, he argues for the concept of a caged complex which is an electronically unstable intermediate held together by the surrounding solvent molecules for a time sufficient for configurational changes to occur. The major conclusions of his study for the T-for-H substitution in the gas and condensed phase occurs predominately with retention of configuration, possibly, according to the impact model. In the gas phase, Cl-for-Cl substitution occurs predominately with retention of configuration, possibly according to the impact model. However, Stöcklin feels that neither the impact model nor radical caging reactions satisfactorily explains the liquid state results; instead he assumes a caged intermediate whose lifetime is effectively prolonged by the surrounding molecules.

So far, we have seen Richardson and Wolfgang for fluorine reactions, Rack and his co-workers for bromine reactions, and Welch and his group for iodine reactions involving both molecular and caging mechanisms for the liquid state

reactions. Dr. Stöcklin suggests for chlorine reactions the concept of substitution via a caged complex.

It is my opinion that satisfactory progress is being made on all fronts in the gas to condensed phase transition. Many more experiments are required, especially of the kind performed by Dr. Stöcklin's group. However, after a period of time, in order to project a viable image to the outside community, it is important that we come to some kind of mutual agreement as to what are the most logical events occurring in the liquid state.

In such a short time, it is impossible to present in any detail other significant work by others. This includes the very interesting studies of Professor Ache's group involving electrophilic gas phase substitution reactions of bromine ions with halomethanes and his stereochemistry experiment in collaboration with Dr. Stöcklin involving decay-induced halogen exchange in diastereomeric 2,3-dichlorobutanes. Dr. Tachikawa is continuing his investigations of gas phase bromine reactions activated by radiation neutron capture and isomeric transition in various alkanes and halomethanes making important contributions in this area.

1. CHEMICAL ACCELERATORS

- (a) atom-molecule
- (b) ion-molecule

2. BULB TECHNIQUES

- (a) photo chemical recoil
- (b) nuclear recoil

Slide 1

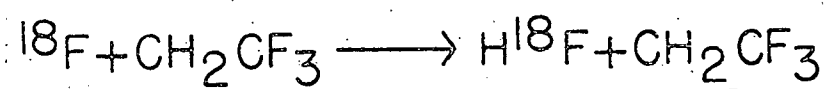
I. DETERMINATION OF PREVIOUSLY
UNKNOWN REACTION MODES QUICKLY
AND INEXPENSIVELY

Slide 2

DETERMINATION OF REACTION MECHANISMS
FOR A GREAT NUMBER OF LOW
PRESSURE, HIGH PRESSURE AND
CONDENSED PHASE SYSTEMS

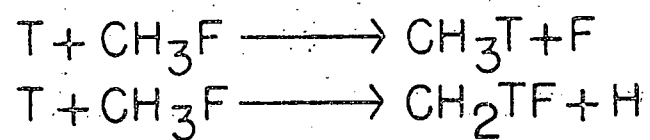
Slide 3

ABSTRACTION



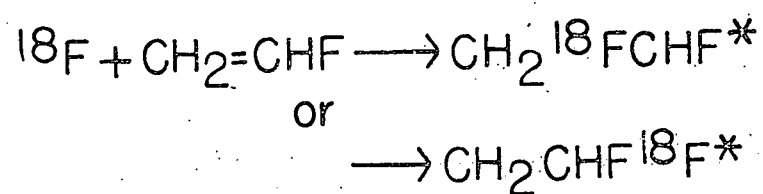
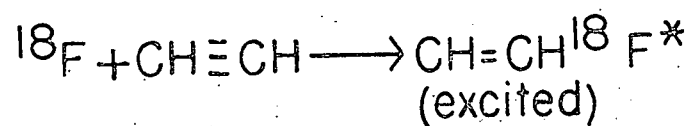
Slide 4

SUBSTITUTION FOR ANOTHER ATOM
(H, D, X) OR RADICAL (CH₃, etc)



Slide 5

ADDITION TO UNSATURATED
BONDS SUCH AS OLEFINS AND
ACETYLENES YIELDING HIGHLY
EXCITED RADICALS.



STUDIES INVOLVING GAS
TO CONDENSED PHASE TRANSITION
IN HOT ATOM CHEMISTRY

Slide 7

LIBBY'S BILLIARD-BALL COLLISION AND
BILLIARD-BALL COLLISION-EPITHERMAL COLLISION
HYPOTHESIS

WILLARD'S "RANDOM FRAGMENTATION" HYPOTHESIS

GEISSLER-WILLARD "AUGER ELECTION REACTION"
OR AUTO RADIATION-HYPOTHESIS

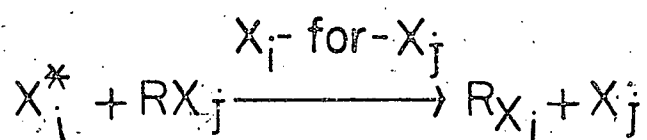
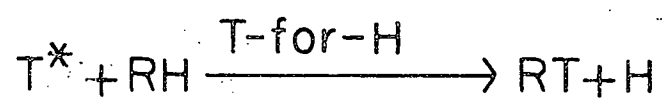
SHAW'S THERMAL SPIKE MODEL

MILMAN'S MODIFIED IMPACT ON MOLECULE MODEL

STÖCKLIN CAGED COMPLEX MODEL

COMBINATION MOLECULAR AND CAGED
RADICAL REACTIONS

STEREO CHEMISTRY OF SUBSTITUTION REACTIONS



PREVIOUS RECOIL T-FOR-H SUBSTITUTION STUDIES
AT ASYMMETRIC CARBON ATOMS

Phase	Molecule Studied	Asymmetric Carbon Substitution Product	Retention (%)
Solid	Glucose	Glucose Galactose	99
	L-Alanine	L-Alanine D-Alanine	95
	d1-DCB ^a	d1-DCB meso-DCB	95.5
Liquid	Glucose	Glucose Galactose	90
	d1-DCB	d1-DCB meso-DCB	97.7
	d1-DCDFE ^b	d1-DCDFE meso-DCDFE	80.4
	meso-DCDFE	meso-DCDFE d1-DCDFE	94
	d1-DCDFE	d1-DCDFE meso-DCDFE	80
	meso-DCDFE	meso-DCDFE d1-DCDFE	92

Phase	Molecule Studied	Asymmetric Carbon Substitution Product	Retention (%)
Gas	D-2-Butanol	D-2-Butanol L-2-Butanol	90
	L-2-Butanol	L-2-Butanol D-2-Butanol	95
	d1-DCB	d1-DCB meso-DCB	93
	meso-DCB	meso-DCB d1-DCB	80
	d1-DCDFE	d1-DCDFE meso-DCDFE	97.6
	meso-DCDFE	meso-DCDFE d1-DCDFE	99.5
	d1-DCDFE	d1-DCDFE meso-DCDFE	96
	meso-DCDFE	meso-DCDFE d1-DCDFE	96

a DCB = 2,3-Dichlorobutane

b DCDFE = 1,2-Dichloro-1,2-Difluoroethane

IMPACT MODEL

1. FAST, DIRECT DISPLACEMENT
2. INDEPENDENT OF BOND STRENGTHS
3. DEPENDENT ON POINT AND DIRECTION OF IMPACT (STERIC FACTORS)

INERTIAL MODEL

Hot atom reactions requiring relaxation motions that are slow compared to the time of collision tend to be forbidden.

- A. Substitution is affected by the presence of substituents other than that being displaced.
- B. Substitution yields are related to the ability of the target molecule to rotate rapidly
- C. Inertial effects are of a greater magnitude than steric factors.

PREVIOUS RECOIL HALOGEN X-FOR-Y SUBSTITUTION STUDIES
OF ASYMMETRIC CARBON ATOMS

Phase	Recoil Halogen	Molecule Studied	Asymmetric Carbon Substitution Product	Retention (%)
Solid	^{38}Cl	dl-DCB ^a	dl-DCB meso-DCB	50
	^{38}Cl	meso-DCB	meso-DCB dl-DCB	60
Liquid	^{38}Cl	dl-DCB	dl-DCB meso-DCB	74
	^{38}Cl	meso-DCB	meso-DCB dl-DCB	70
	$^{80\text{m}}\text{Br}$	dl-DCB	threo-BCB ^b erythro-BCB	92
	$^{80\text{m}}\text{Br}$	meso-DCB	erythro-BCB threo-BCB	95
	^{18}F	dl-DCB	threo-FCB ^c erythro-FCB	73.2

Phase	Recoil Halogen	Molecule Studied	Asymmetric Carbon Substitution Product	Retention (%)
Liquid	^{38}Cl	d1-DCB	d1-DCB meso-DCB	74.5
	$^{80\text{m}}\text{Br}$	d1-DCB	threo-BCB erythro-BCB	58.3
	^{126}I	d1-DCB	threo-ICB ^d erythro-ICB	54
Gas	^{38}Cl	d1-DCB	d1-DCB meso-DCB	93
	^{38}Cl	meso-DCB	meso-DCB d1-DCB	95
	^{38}Cl	d1-DCB	d1-DCB meso-DCB	93
	^{38}Cl	meso-DCB	meso-DCB d1-DCB	95
	^{18}F	d1-DCDFE ^e	d1-DCDFE meso-DCDFE	90
Gas	^{18}F	meso-DCDFE	meso-DCDFE d1-DCDFE	90
	$^{80\text{m}}\text{Br}$	d1-DCB	threo-BCB erythro-BCB	90
	^{38}Cl	d1-DCDFE	d1-DCDFE meso-DCDFE	91
	^{38}Cl	meso-DCDFE	meso-DCDFE d1-DCDFE	92

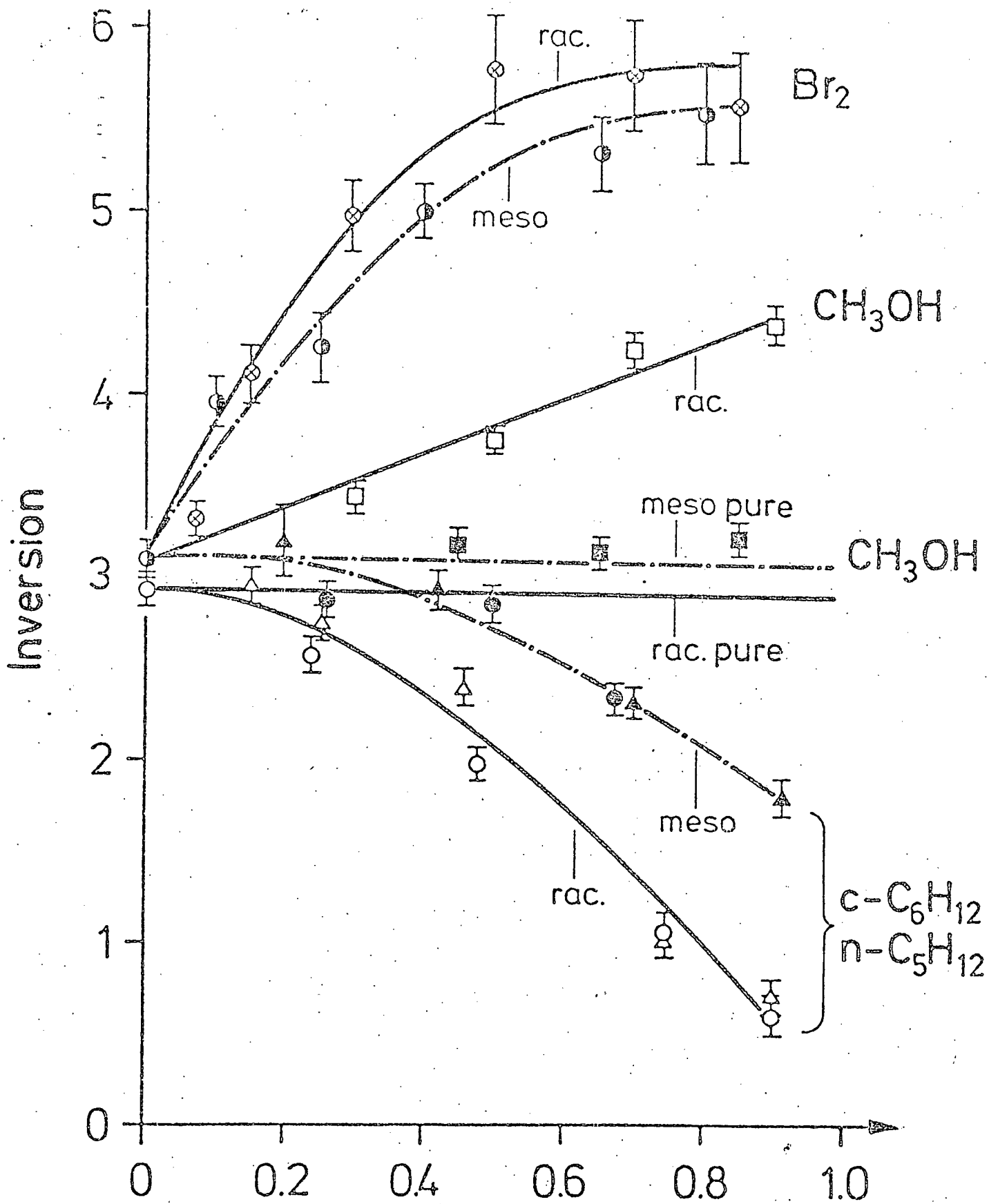
a DCB = 2,3-Dichlorobutane

b BCB = 2-Bromo-3-Chlorobutane

c FCB = 2-Fluoro-3-Chlorobutane

d ICB = 2-Iodo-3-Chlorobutane

e DCDFE = 1,2-Dichloro-1,2-Difluoroethane

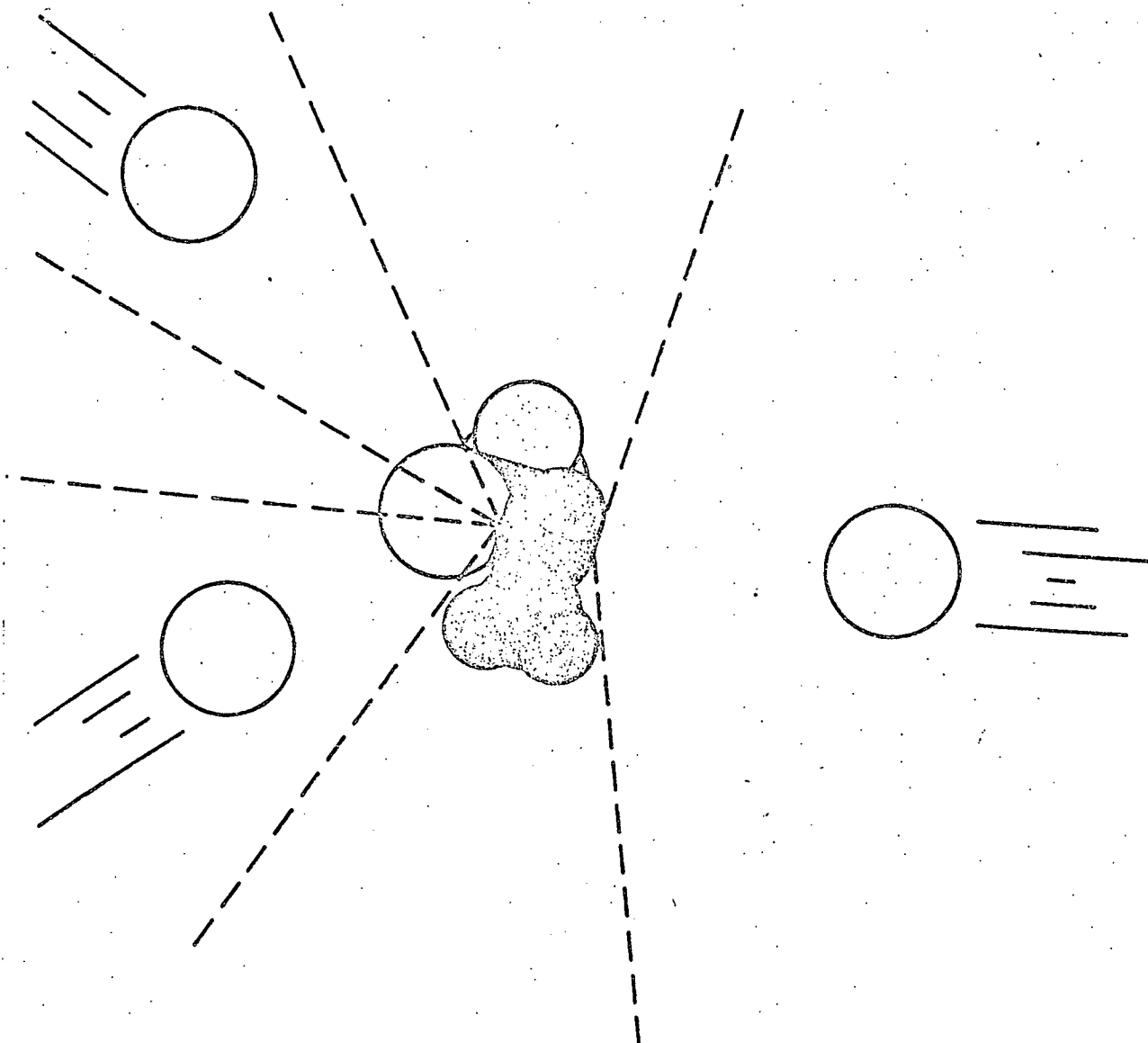


Mole Fraction of Solvents
 VASAROS, MACHOLLA AND STOCKLIN (1972)

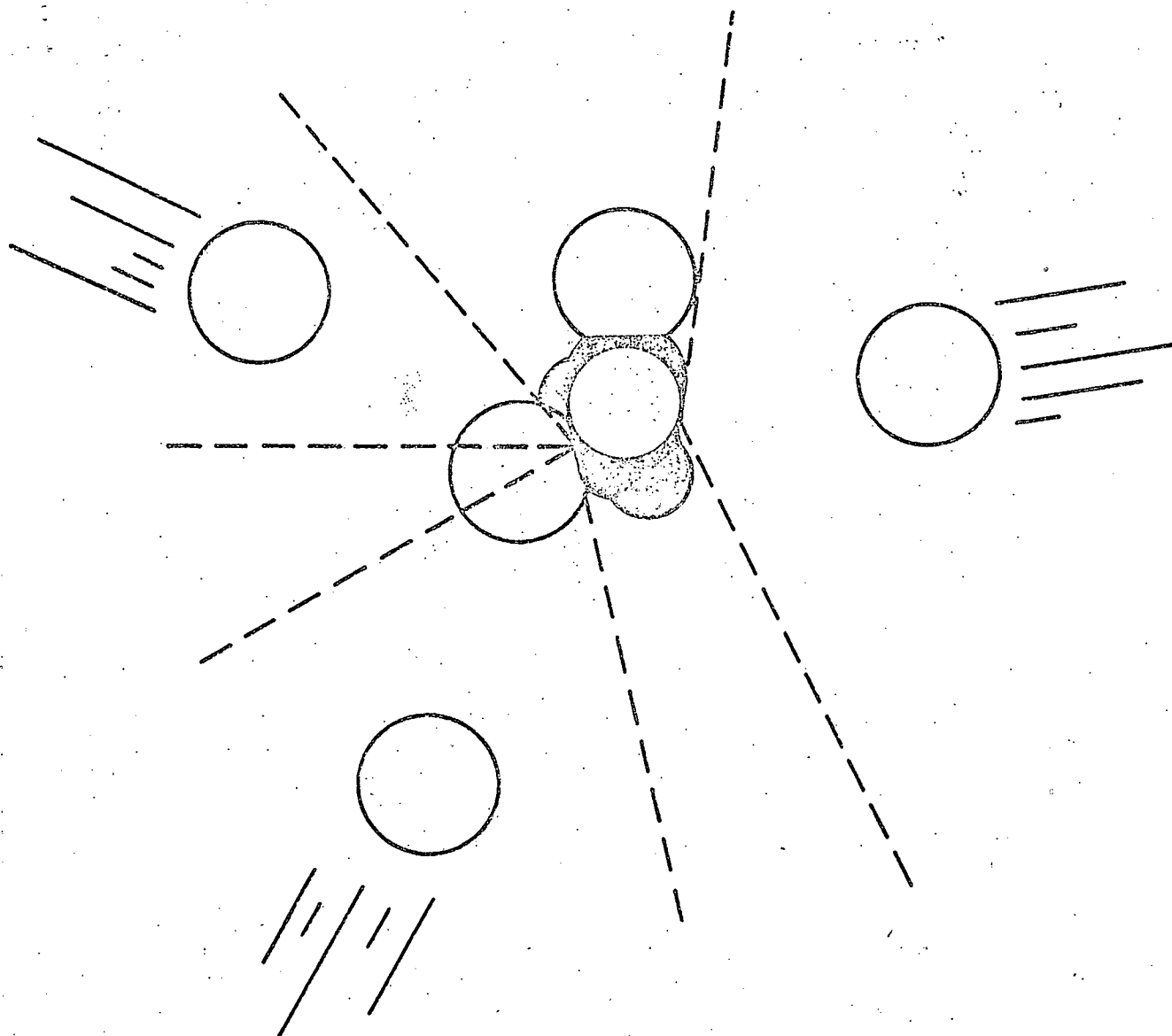
YIELDS OF ^{38}Cl and $^{34\text{m}}\text{Cl}$ -FOR-CL SUBSTITUTION AT THE ASYMMETRIC CARBON OF
 2(R)-(-)- AND 2(S)-(+)-CHLOROPROPIONYL CHLORIDE IN THE GAS PHASE AT +110 C

Enantiomer	Pressure Torr	Nuclide	Absolute Yield %	Retention %	Inversion ¹ %	Ratio Retention to Inversion
S-(+)	590	^{38}Cl	1.0±0.1	17.7±8.0	82.3±8.0	0.21±.13
R-(-)	590	^{38}Cl	1.0±0.1	20.0±7.3	80.8±7.3	0.25±.12
S-(+)	400	$^{34\text{m}}\text{Cl}$	1.3±0.1	18.8±2.0	81.2±2.0	0.23±.03
R-(-)	400	$^{34\text{m}}\text{Cl}$	1.3±0.1	21.3±2.0	78.7±2.0	0.27±.03

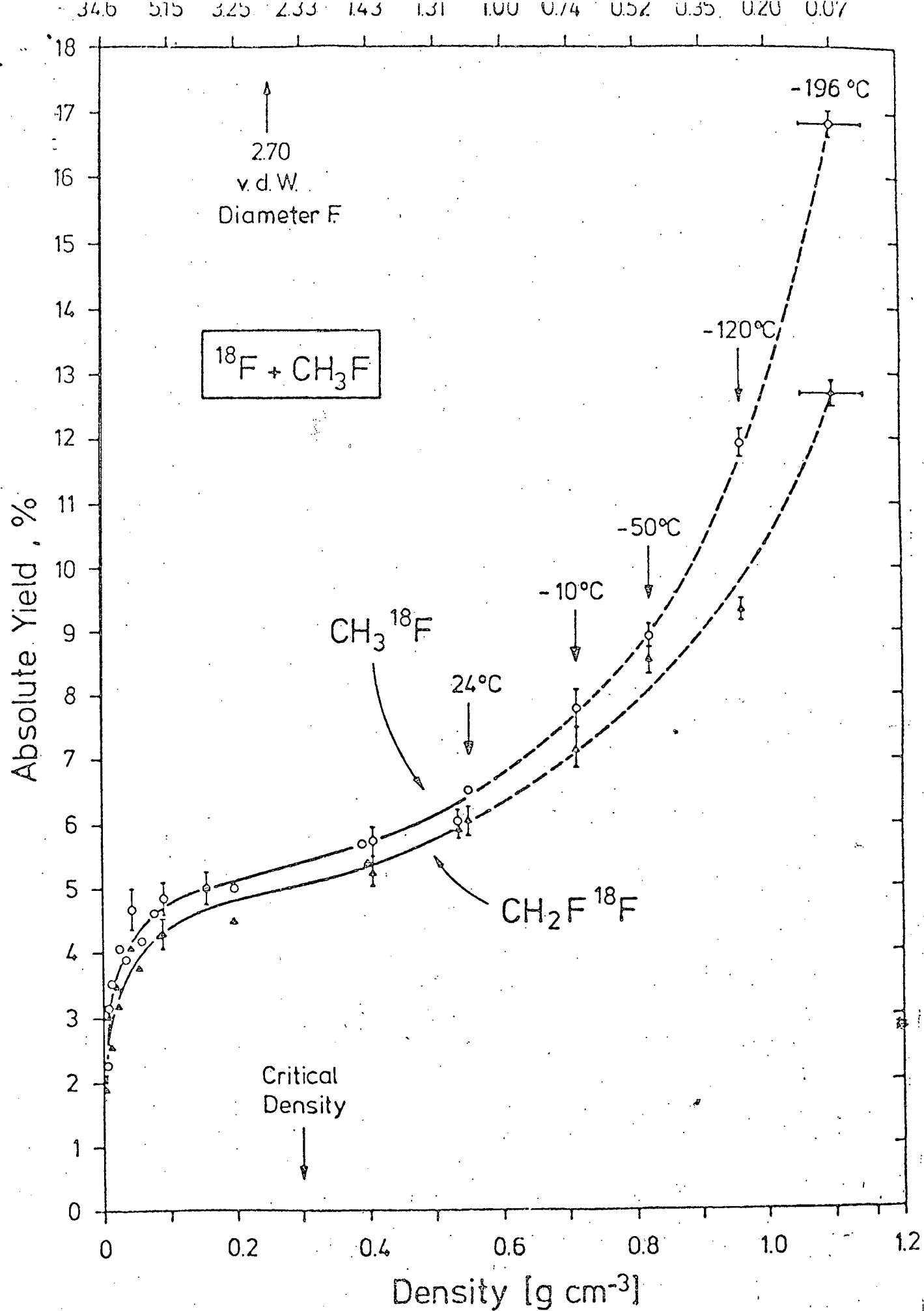
WOLF, PETTIJOHN AND RACK

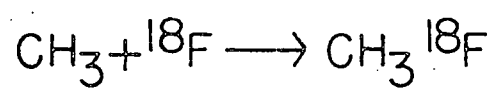


Substitution trajectories required for retention and inversion during a Cl-for-Cl substitution in 2-chloropropionyl chloride in the gauche prime conformation.

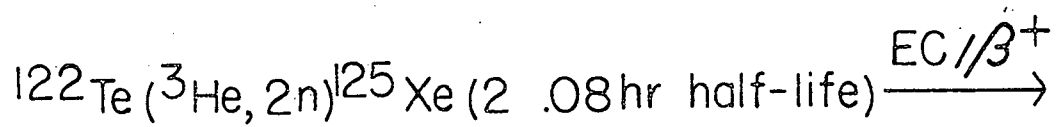


Substitution trajectories required for retention and inversion during a Cl-for-Cl substitution in 2-chloropropionyl chloride in the gauche prime conformation.

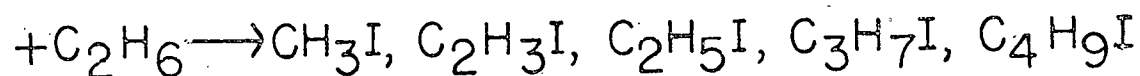
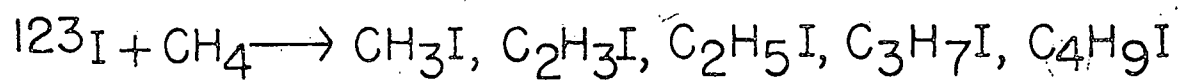


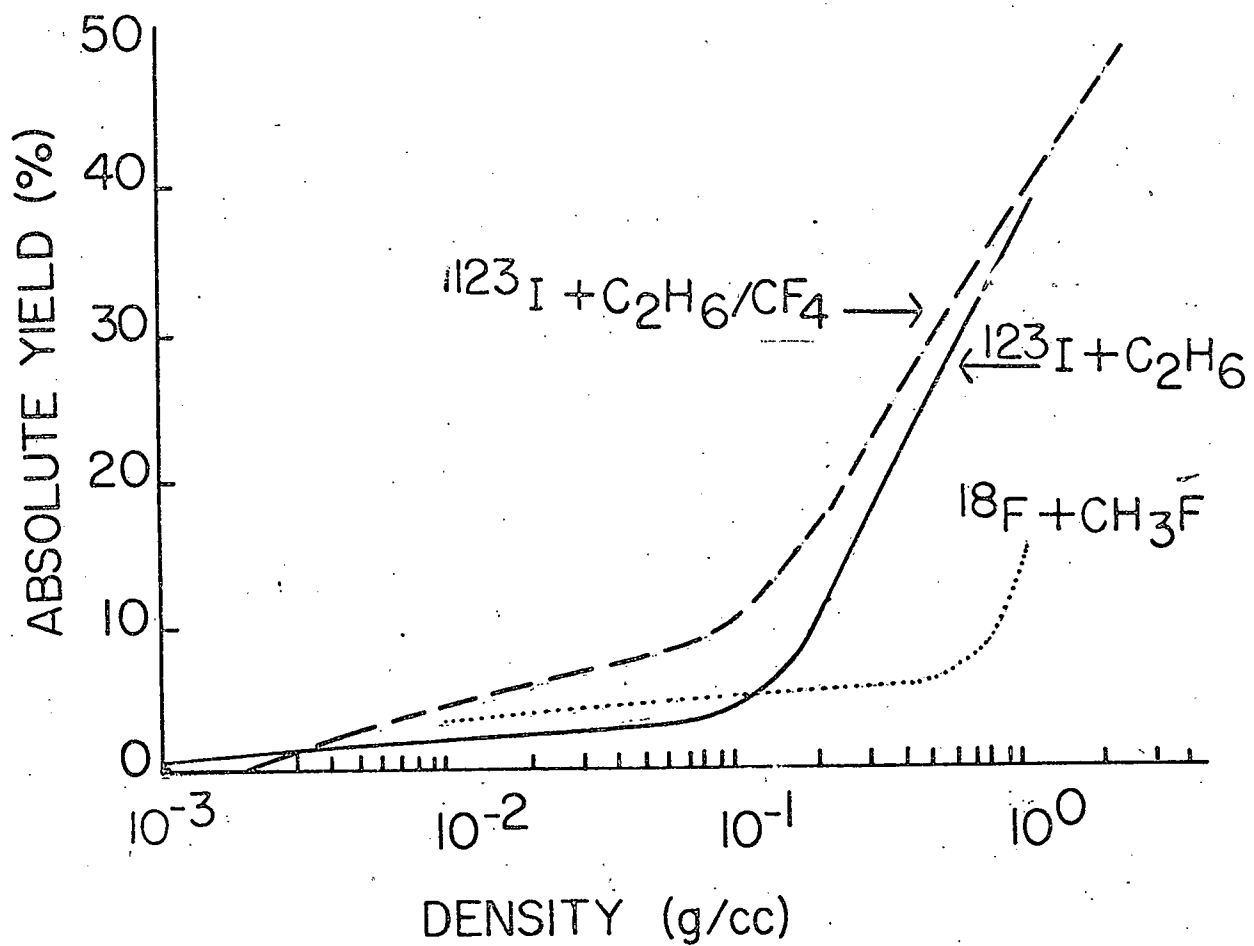


Slide 21



^{125}I (13.3 hr. half-life)





LOBERG, KROHNA, AND WELCH (1973)

