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~~Appendix II~~
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On the Stereochemistry of the Decay-Induced Halogen Exchange in Diastereomeric Alkylhalides in the Gasphase[1]

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Abstract

The stereochemistry of the halogen for halogen substitution at asymmetric carbon atoms, induced by energetic or thermal bromine and iodine species was studied in diastereomeric alkylhalide molecules such as d,l- and meso-2,3-dichlorobutane.

Energetic ^{80}Br species were generated via the ^{80m}Br(I.T.)^{80}Br nuclear process in reactor produced $CF_3{}^{80m}Br$ and allowed to react with the substrate molecules while still possessing excess kinetic energy or after having become thermalized in collisions with argon atoms. ^{125}I species were produced via the radioactive decay of ^{125}Xe.

The observed results show in unmoderated systems generally a predominance of those products which were formed in the halogen for halogen exchange process under retention of configuration.

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In the presence of excess argon, however, the degree of stereospecificity of the reaction seems to vary with the type of diastereomer used as substrate. In the case of 2,3-dichlorobutane the ratio of product formed via retention to that formed via inversion is approximately 0.4 if a d, l mixture is the substrate, whereas the corresponding ratio increases only slightly to 3.1 if the meso diastereomer is used.

An attempt will be made to interpret the results by assuming a substitution mechanism involving an electrophilic attack of Br^+ ions at the asymmetric carbon atoms.

Introduction

Previous work by several investigators has suggested that a considerable fraction of the halogen species generated via the nuclear decay $^{80m}Br \xrightarrow{I.T.} {}^{80}Br$ or $^{125}Xe \xrightarrow{E.C.} {}^{125}I$ reacts as thermal ionic species with organic substrate molecules in the gasphase.[2-12] This is quite different from the hot homolytic substitution reactions carried out by nucleogenic tritium and halogen atoms following (n,γ) or other highly exothermic nuclear reactions, where the recoil species lose their initial charge very quickly and react predominantly as neutral atoms.[13]

Thus it seems that the study of the reactions of decay induced halogen species could significantly contribute to our knowledge of the detailed reaction mechanisms and parameters involved in electrophilic substitution reactions of simple hydrocarbons in the gasphase. It appears that this technique can be of special importance in cases where other methods such as ion cyclotron resonance or high pressure mass spectrometry cannot provide the necessary information, i.e. in cases where one wishes to study the stereochemistry of the reaction or where several isomers may result from the substitution. An interesting application of this technique is the recent investigation by Cacace and Stöcklin[7] in which they studied the isomer distribution following the electrophilic attack of halogen in various benzene derivatives.

In the present study we tried to assess the stereochemical course of the decay induced halogen for halogen substitution following $^{80m}Br \xrightarrow{I.T.} {}^{80}Br$ and $^{125}Xe \xrightarrow{E.C.} {}^{125}I$ in meso and d,l-2,3 dichlorobutane in the gasphase under various experimental conditions. An attempt will be made to explain the observed results in terms of a mechanism which involves an electrophilic (front side) attack of the halogen ion at the asymmetric carbon atom leading to the formation of a relatively longlived complex which may undergo subsequently racemization. This mechanism is similar to the mechanism recently proposed by Cacace[14] for the gasphase electrophilic attack of gaseous Brønsted acids at asymmetric carbon atoms.

Experimental Section

Materials:

CF_3Br, CH_2=CH-CH=CH_2, Cl_2 and O_2 were obtained from Matheson Chemical Co. with a stated purity level greater than 99.0%. Argon and xenon with a stated purity level of 99.999% were purchased from Air Reduction Co. and used without further purification. The meso and d,l forms of dichlorobutane were prepared by stereospecific addition of Cl_2 to trans- and cis-butene-2 respectively.[15]

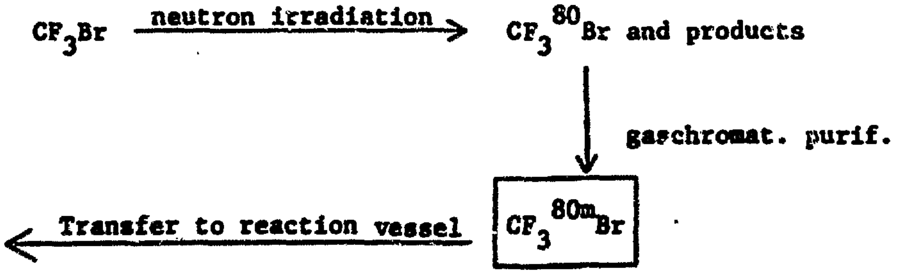
The products were purified by gas chromatography, using 4m glass columns (5 mm i.d.) with 20% DEGS on Chromosorb W, 60-80 mesh at 80°C and 100 cc He/min. Similarly, the diastereomers of 1 bromo-2,3 dichlorobutenes, and the diastereomers of 2 bromo,2,3 dichlorobutanes were obtained by stereospecific addition of Cl_2 to cis and trans 1 and 2 bromo-butene-2, (purchased from K & K) respectively. Purification was achieved by gas chromatography on the columns described above at 110°C.

Erythro- and threo-2 bromo 3 chlorobutane and 2 iodo 3 chlorobutane which were used in small amounts as carriers were prepared following procedures described in the literature[16-18] and subsequently gas chromatographically purified.[19]

Preparation of ^{80}Br Source

CF_3Br was preferentially used as the ^{80}Br source because of its ionization potential of 12.3 eV, which lies above that of Br^+ and thus would not interfere with the Br^+ reaction by charge transfer.

The procedure is schematically as follows:



A few mg of CF_3Br were sealed in a quartz capillary and irradiated in the VFI and SU Nuclear Reactor at a flux of about 10^{12}n cm^{-2} sec^{-1} for 30 minutes at 40°C. After the reactor irradiation the contents of the quartz ampoule were subjected to gaschromatographic purification on a 2m Poropak Q column. The CF_3Br fraction, containing ^{80m}Br-, ^{80}Br-, and ^{82}Br-labeled CF_3Br formed during the irradiation was trapped and transferred to the reaction vessel.[20]

Preparation of ^{125}Xe

Appropriate amounts of Xe sealed in quartz ampoules were neutron irradiated in the FRJ-1 nuclear reactor of the Nuclear Research Center, Juelich, and subsequently transferred into the reaction vessel. The neutron flux was 5×10^{12} cm^{-2} sec^{-1} for a period of 1 h.

Preparation of Reaction Mixture

The reaction was carried out in a spherical, specifically designed, pyrex glass vessel with a total volume of 500 ml. In- and outlet valves were Kontes' greaseless high vacuum valves.

The vessel was filled by the usual vacuum line technique with the desired amounts of reactants.

In the case of the Br^+ investigation the reaction mixture was allowed to stand (in the dark, at room temp.) for 100 minutes to permit the ^{80}Br to attain equilibrium with the ^{80m}Br while in the reaction vessel.

In the case of the $^{125}I^+$ experiments the exposure time was 70 minutes at room temperature.

Sample Analysis

At the end of the reaction the ^{80}Br or ^{125}I labeled products were collected in traps at liquid nitrogen temperature and appropriate amount of carriers dissolved in CH_2Cl_2 added. The resulting solution was washed first with aqueous (dil.) Na_2SO_3 solution then with dist. water and dried. The analysis of the ^{80}Br or ^{125}I labelled products was accomplished by a discontinuous radiogaschromatographic technique.[20,21]

Columns used were either a 4 m glass column (5 mm i.d.) with 20% DEGS on Chromosorb W 60-80 mesh, temperature programmed, or a 8 m glass column (5 mm i.d.) 15% SF-96 on Chromosorb W, 60-80 mesh operated at 80°C. The latter column was used for the separation of the diastereomeric 2 iodo-3-chlorobutanes.

Radioactivity Assay

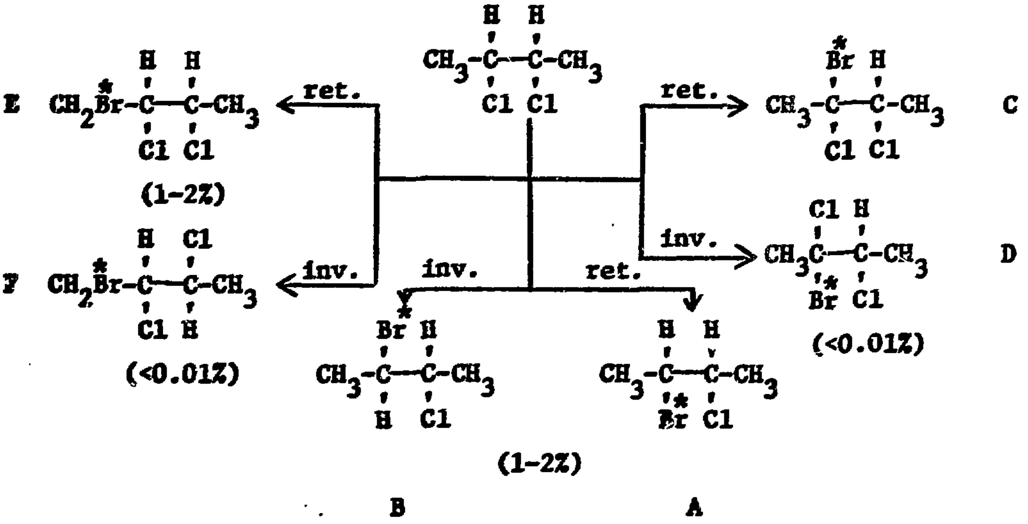
The separated radioactive products were directly trapped from the effluent gas stream by bubbling the effluent gas from the gaschromatograph through toluene solutions containing liquid scintillation fluors. More than 99% of all the reaction products identified in this investigation were retained in the solution, with the exception of CF_3Br, for which calibration runs were carried out and appropriate corrections made.[20]

The ^{125}I or ^{80}Br- counting was done by liquid scintillation spectrometry applying appropriate energy discrimination. The yields of the products, i.e. the ratio of the ^{80}Br-activity present at the end of the reaction in each individual product to the total ^{80}Br-activity (at end of the reaction) were computed by using the well known equations for radioactive decay and growth.

Results and Discussion

Several series of experiments were carried out to identify the products resulting from the reaction of ^{80}Br and ^{125}I species generated in the nuclear decay of ^{80m}Br or ^{125}Xe with meso and d,1 2,3 dichlorobutane as substrate in the gas phase and to determine their relative radiochemical yields.

Of particular interest for this study were the ^{80}Br or ^{125}I substitution products derived from the two diastereomers of the 2,3 dichlorobutane substrate molecules, which include in the case of meso 2,3 dichlorobutane the following products as shown schematically:



(numbers in parentheses are the radiochemical yields in % of total ^{80}Br formed in reaction mixture)

1.) The erythro-2 bromo 3 chlorobutane, as a result of ^{80}Br for Cl substitution under retention of configuration (A)

2.) the threo-2 bromo 3 chlorobutane as a result of ^{80}Br for Cl substitution under inversion of configuration

3.) the two diastereomers resulting from ^{80}Br for H substitution (with (C) or without (D) retention of configuration).

4.) the products formed as a result of ^{80}Br for H substitution in one of the methylgroup (E and F) (Product: the diastereomers of 1 bromo-2,3 dichlorobutane).

(Corresponding products are formed following ^{80}Br substitution in the d,1 form of 2,3 dichlorobutane)

Previous ^{80}Br substitution experiments[20] with substrate molecules such as CH_3Cl or CH_2Cl_2 have already indicated that the probability of ^{80}Br for H substitution in molecules where the ^{80}Br is given a choice to substitute either a H or Cl (attached to the same carbon atom) is very small compared with ^{80}Br for Cl substitution.

A similar trend was observed in the present study where the yields of the 2 bromo-2,3 dichlorobutane were found to be too small to (<0.01%) allow a reasonable determination of the amount of ^{80}Br incorporated into each of the two diastereomers.

Interesting seems to note that in the case of ^{80}Br for H substitution in the methyl group leading to the 1 bromo-2,3 dichlorobutanes which proceeds with a relatively good yield (about 1-2% of all ^{80}Br produced is found in this compound), ^{80}Br is found in each ease exclusively in the product which has retained its original configuration at the two asymmetric centers.

Thus in the following only the relative yields of the products resulting from halogen for halogen substitution will be reported and discussed.

In the first series of experiments the effect of moderator, in this case argon, on the stereochemical course of the ^{80}Br for Cl substitution in meso and d,l dichlorobutane was studied in the gas phase. The reaction was carried out in a 500 ml pyrex vessel containing 12 torr of the substrate, 15 torr of $CF_3{}^{80m}Br$, which served as the source of ^{80}Br, and 20 torr O_2 as scavenger. Various amounts of argon were added to this mixture; the reaction time was 100 min. The results are shown in figure 1, where the ratio of retention to inversion, i.e. the ratio of the relative amounts of ^{80}Br found in the 2 bromo 3 chlorobutane molecule formed under retention and inversion of configuration, respectively, is plotted as a function of the mole % argon present and the total pressure of the system. The results clearly suggest that when meso-2,3 dichlorobutane is the substrate argon additives have only a minor effect on the ratio of retention to inversion, i.e. on the relative yields of ^{80}Br labeled erythro and threo 2 bromo 3 chlorobutane, whereas when the d,l form is the substrate under the same experimental conditions a drastic reduction of this ratio, representing the relative yields of ^{80}Br labelled threo to erythro 2 bromo 3 chlorobutane can be observed.

Since in this series of experiments the moderator concentration was increased by adding additional argon to the reaction mixture which was consistently made up of about 12 torr of substrate, 20 torr of CF_3Br and 20 torr O_2 the total pressure of the system increased simultaneously from about 50 to 1000 Torr. Thus the observed effect could be due to either one of the two parameters: increased total pressure or increased argon concentration or both.

The effect of total pressure within the above range on the stereochemistry of the halogen exchange was tested in a second series of experiments, where the composition of the reaction mixture which included 94 Mole % argon was kept constant, while the total pressure was changed. The fact that within the pressure range under investigation no change in the retention to inversion ratio was observed, as shown in Figure 2 for the various systems (for experimental conditions see fig. 2) where the ratio retention/inversion is plotted as a function of the total pressure,

clearly indicates that under these experimental conditions the system is relatively insensitive to an about tenfold change in total pressure. The variations in the retention to inversion ratio found in the ^{80}Br-d,l 2,3-dichlorobutane system must therefore be associated with the presence of increasing amounts of argon.

This contention was further borne out in another series of experiments done at constant pressure (15 Torr) in which d,l 2,3 dichlorobutane was again the substrate, however, the nuclear process used to generate the halogen species was $^{125}Xe \xrightarrow{E.C.} {}^{125}I$ and thus the halogen for halogen substitution products were now the diastereomers of 2 chloro-3 iodobutane, xenon was also used as moderator. The trend displayed by the results as shown in figure 3, where also the exact experimental conditions can be found,is very similar to that observed in the corresponding substitution reactions with ^{80}Br as the reactant, although the absolute radiochemical yields are somewhat lower,0.2% vs 1-2% in the case of Br substitution.

It seems that the retention to inversion ratio again approaches a limiting value of about 0.5, which is very close to the corresponding value (0.4) postulated for the ^{80}Br substitution. The results may then be summarized as follows:

1.) The ratio retention/inversion is not pressure dependent in the range from 50-1000 torr.

2.) The ratio retention/inversion is affected by the addition of moderator only to a small extent if meso-DCB is the substrate and approaches a limiting value of approx. 3.2.

3.) The ratio retention/inversion decreases drastically with increasing moderator concentration if dl-DCB is the substrate, approaching a value of about 0.4-0.5. This effect seems to be independent of the type of nuclear reaction: ($^{80m}Br \xrightarrow{I.T.} {}^{80}Br$ or $^{125}Xe \xrightarrow{E.C.} {}^{125}I$) and the nature of the rare gas (Ar or Xe) used as moderator.

These findings clearly indicate that the stereochemical course of the nuclear decay induced halogen for halogen substitution leads to results considerably different from those observed with the same substrates when the substituting halogen species is ^{38}Cl or ^{39}Cl produced in the highly exothermic $^{37}Cl(n,\gamma)^{38}Cl$ or $^{40}Ar(\gamma,p)^{39}Cl$ nuclear processes. In these latter investigations carried out by Rowland et.al.[22-23] it was found that ^{38}Cl (or ^{39}Cl) for Cl substitution results overwhelmingly in the formation of products obtained under retention of configuration if 1,3 butadiene was present as radical scavenger. In absence of 1,3 butadiene the ratio changed favoring the thermodynamically more stable erythro product with increasing amounts of argon added to the system. The authors tried to rationalize this effect with the contribution of radical recombination reactions becoming more significant at higher moderator concentrations.

In the present study the addition of moderator leads to a change of the product ratio again in favor of the thermodynamically more stable erythro enantiomer[23] as shown in figure 4, where the ratio of ^{80}Br labeled erythro to threo 2 bromo 3 chlorobutane is plotted as a function of argon concentration (same experimental conditions as described in figure 1).

We, therefore, very carefully examined the possibility of radical recombination reactions affecting our results, by adding 1,3 butadiene, which was found to be very efficient to suppress these radical reactions in the Rowland and Wai study,[23] to the reaction mixture.

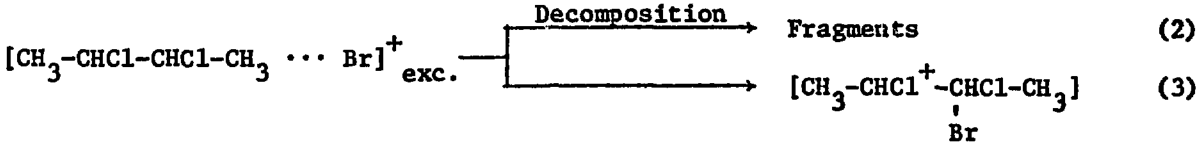
The results, as summarized in table I, do not show any significant effect of the added 1.3 butadiene on the product ratio which would have supported the presence of radical recombination mechanisms contributing to the overall substitution under these experimental conditions. Thus other possible explanations will have to be discussed.

One basic difference between the halogen species produced via (n,γ) or other highly exothermic nuclear reactions and via a nuclear decay is that in the former case the initially charged halogen ion undergoes a sufficiently large number of collisions with the surrounding matter to lose its charge long before it reacts chemically, this will be true also in the presence of excess rare gases.[13] On the other hand, the halogen, generated in the nuclear decay, is also formed as a highly charged species,[24] however, it usually acquires much less kinetic energy (as a consequence of the nuclear decay process) and is more likely to reach thermal energies before it becomes completely neutralized,[9] this even more so if the surrounding matter, such as argon or xenon, has an ionization potential which lies between the first and second ionization potential of the bromine (or iodine).

Thus it seems to be highly probable that in the present study, especially at the highest moderator concentrations used, where no hot reactions could occur anymore, the reacting species is a singly charged Br^+ or I^+.

Thus in analogy with previous studies[7,20,25] on the electrophilic reactions of Br^+, one can postulate a reaction mechanism in which the $^{80}Br^+$ ions attack the substrate yielding excited ions (1), that can either decompose (2), or become stabilized (3):

$$^{80}Br^+ + CH_3\text{-}CHCl\text{-}CHCl\text{-}CH_3 \rightarrow [CH_3\text{-}CHCl\text{-}CHCl\text{-}CH_3 \cdots Br]^+_{exc} \qquad (1)$$



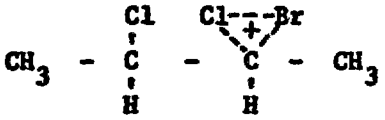
$$[CH_3\text{-}CHCl\text{-}CHCl\text{-}CH_3 \cdots Br]^+_{exc.} \xrightarrow{\text{Decomposition}} \text{Fragments} \qquad (2)$$

$$[CH_3\text{-}CHCl\text{-}CHCl\text{-}CH_3 \cdots Br]^+_{exc.} \longrightarrow [CH_3\text{-}\underset{\displaystyle Br}{CHCl^+}\text{-}CHCl\text{-}CH_3] \qquad (3)$$

followed by elimination of a proton or halide ion, most likely by transfer to another substrate molecule, yielding the final reaction product.

If one adopts this mechanism several possibilities could then account for the results observed in this study:

1) The halogen species makes its attack exclusively from the front side resulting in the formation of a compound with a three centered bond structure,[14,26,27]



$$CH_3 - \overset{Cl}{\underset{H}{C}} - \overset{Cl \cdots \overset{+}{} \cdots Br}{\underset{H}{C}} - CH_3$$

yielding a substitution product which retains the original configuration. In this case to account for the considerable amount of inversion occurred one would have to postulate that the resulting complex survives immediate decomposition, i.e. its energy contents is not exceedingly high, however, the complex has sufficient energy for racemization to occur during the lifetime of the complex. The lifetime of the complex will depend on its energy contents and on the availability of a (gaseous) Brønsted base to act as an acceptor for the chlorine ion which has to be removed from the complex.

Thus in order to test this possibility one would have to add very efficient energy sinks, which would quickly remove any excess energy from the complex, or strong Brønsted bases to initiate a quick Cl^+ transfer, i.e. to reduce the possibility for racemization either by deactivation of the complex or by shortening the lifetime of the complex.

An initial experiment in this direction was done by adding small amounts of methanol (vapor), which is known to be a good energy sink and a relatively strong Brønsted base, to the system. The results, listed in table I, show a drastic increase in retention to inversion ratio if d,l 2,3 dichlorobutane are the substrate and Br^+ the electrophile.

These results, although they should be considered as tentative results, seem to support the above explanation which assumes racemization to occur during the lifetime of the molecule ion complex, formed by frontside attack of the electrophile. Further evidence for this mechanism may be seen in the fact that in both systems the ratio of erythro to threo product observed is close to the thermodynamic equilibrium concentration of the two diastereomers.

2) An alternate explanation may be that the product ratio observed in this study is determined by the initial approach of the electrophile i.e. front- or back-side attack at the substrate, which, in turn, may be subject to strong conformational steric effects.

Recent results obtained in the case of hot chlorine substitution in racemic or meso 2,3 dichlorobutane in the liquid phase or in solutions[28], where a considerable amount of the inverted product was observed, were interpreted by assuming two channels for hot substitution: (1) a direct replacement without change in configuration and (2) a back side attack leading to inversion. The relative cross sections for these two reaction channels seem to depend on the steric suitability of each compound for front- or backside attack by the halogen and thus on the equilibrium concentration of the various conformers present under the given experimental conditions.

On the other hand halogen for halogen substitution occurs overwhelmingly with retention of the original configuration if carried out in the gas phase.[22-23,28] Rowland and coworkers[29] interpreted this result by assuming that hot substitution via inversion (i.e. backside attack), if it occurs at all, involves an excessive amount of vibrational energy resulting in a rapid decomposition of of the inverted product in the gasphase, where in contrast to the condensed phase no immediate collisional deactivation is possible.

This was questioned by Stöcklin et al.[30] on the basis of pressure experiments in gaseous systems such as meso or racemic CHCl=CHF, which showed no significant change of the relative amounts of inversion product formed over a relatively wide range of pressure and, therefore, did not support the assumption of a preferential decomposition of the intermediate leading to the inverted compound.

The alternative, proposed by these authors, suggests that the hot atom approaching from the backside transfers during the collision a momentum to the molecule leading to a further separation of the two entities, thus reducing the probability of a complex formation in the gas phase. In the condensed phase this rapid separation of the two species is slowed down by the surrounding matter thus improving the chances of complex formation.

Both models, however, would predict an increase of product formation via inversion if the attack is made by a less energetic species, as it is the case in the present study, where thermal ions are the reactants. It seems of interest to note that the ratio retention to inversion in the d,l 2,3 dichlorobutane system in the case of the hot Cl for Cl substitution approaches 0.5,[28] if the reaction mixture is a highly diluted solution of rac 2,3 dichlorobutane in c-hexane and pentane. This result resembles strongly the retention to inversion ratio observed in the present gas phase study of the $^{80}Br^+$ for Cl substitution in d,l 2,3 dichlorobutane. Infrared studies[31] reveal that the relative concentration of the various conformers of d,l or meso 2,3 dichlorobutane is nearly the same in highly diluted solutions of c-hexane or n-pentane and in the gas phase respectively.

Similar observations have been made in the case of meso-2,3 dichlorobutane where the corresponding ratios in highly diluted c-hexane are 2.4 (for "hot" Cl for Cl substitution) vs 3.0 (for thermal $^{80}Br^+$ for Cl substitution). Thus in analogy to the mechanism proposed by Stöcklin et al. one might consider the possibility that the present results are also determined by conformational effects.

On the basis of the presently available evidence no decision can be made as to which one or what combination of the two mechanisms described reflects correctly the substitution process.

We hope to be able to answer this question by carrying out further studies using different Brønsted bases and other good energy sinks which would change the rate of energy and Cl^+ or proton transfer and thus affect the lifetime of the postulated complex to test the first mechanism whereas temperature studies which should affect the relative conformer concentration would reveal the contribution of a possible steric conformational effect.

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Table I

SUBSTRATE	ADDITIVES (torr)*				% ^{80}Br in BCB [xx]	
(12 torr)	O_2	Ar	$CH_2=CH-CH=CH_2$	CH_3OH	erythro	threo
meso-DCB	20	760	--	---	78.2	21.8
	20	760	20	---	75.4	24.6
	20	760	--	10	80.2	29.8
dl-DCB	20	760	--	---	70.0	30.0
	20	760	20	---	62.1	37.9
	20	760	--	10	35.6	64.4

* Each sample contains 20 torr $CF_3{}^{80m}Br$.

Experiments were carried out in a 500 ml Pyrex vessel; reaction time was 100 minutes at room temperature.

[xx] Quoted values are the average of 4-5 experiments.

Captions:

Table I:

^{80}Br found in each of the two diastereomers of 2 bromo 3 chlorobutane (BCB) (in % of total ^{80}Br incorporated into BCB) following $^{80m}\text{Br} \xrightarrow{\text{I.T.}} {}^{80}\text{Br}$ in meso- or d,l 2,3 dichlorobutanes (DCB) under various experimental conditions.

Fig. 1.

Ratio of ^{80}Br for Cl substitution product formed via retention to that formed via inversion of configuration plotted as a function of argon concentration and total pressure of the reaction mixture following $^{80m}\text{Br} \xrightarrow{\text{I.T.}} {}^{80}\text{Br}$ in meso- and d,l 2,3 dichlorobutane system. (The reaction products are erythro and threo 2,bromo 3-chlorobutane, respectively) Substrate pressure: 12 torr; $CF_3\,^{80m}Br$: 15 torr, O_2: 20 torr. Reaction volume 500 ml, exposure time 100 min; room temperature.

Fig. 2.

Ratio of halogen for Cl substitution product formed via retention to that formed via inversion of configuration plotted as function of total pressure.

I. $^{80m}\text{Br} \xrightarrow{\text{I.T.}} {}^{80}\text{Br}$ in d,l 2,3 dichlorobutane
Retention: threo-2-bromo 3-chlorobutane
Inversion: erythro - 2 bromo 3 chlorobutane
Composition of reaction mixture: DCB: 1.4%; $CF_3\,^{80}Br$: 1.8%; O_2: 2.5% and Ar: 94.3%.
Reaction volume: 500 ml; exposure time 100 min; room temp.

II. $^{125}\text{Xe} \xrightarrow{\text{E.C.}} {}^{125}\text{I}$ in d,l 2,3 dichlorobutane
Retention: threo- 2 iodo 3 chlorobutane
Inversion: erythro-2 iodo 3 chlorobutane
Composition of reaction mixture: DCB: 4%; Xe: 96%
Reaction volume: 500 ml; exposure time 70 min; room temp.

III. $^{80m}Br \xrightarrow{I.T.} {}^{80}Br$ in meso-2,3 dichlorobutane
Retention: erythro-2 bromo 3 chlorobutane
Inversion: threo-2 bromo 3 chlorobutane
Composition of reaction mixture and experimental conditions same as in I

Fig. 3 Ratio of ^{125}I for Cl substitution products formed via retention to that formed via inversion of configuration plotted as function of mole % xenon present, following $^{125}Xe \xrightarrow{E.C.} {}^{125}I$ in d,1 2,3 dichlorobutane.

Retention: threo-2 iodo 3 chlorobutane

Inversion: erythro-2 iodo 3 chlorobutane

Total pressure of reaction mixture: 15 torr

Reaction volume: 500 ml; exposure time 70 min; room temperature.

Fig. 4 Ratio of ^{80}Br labeled erythro to threo 2 bromo-3 chlorobutane vs mole % argon present in reaction mixture following $^{80m}Br \xrightarrow{I.T.} {}^{80}Br$ in meso and d,1 dichlorobutane. Experimental condition same as described in Fig. 1.

Fig. 1

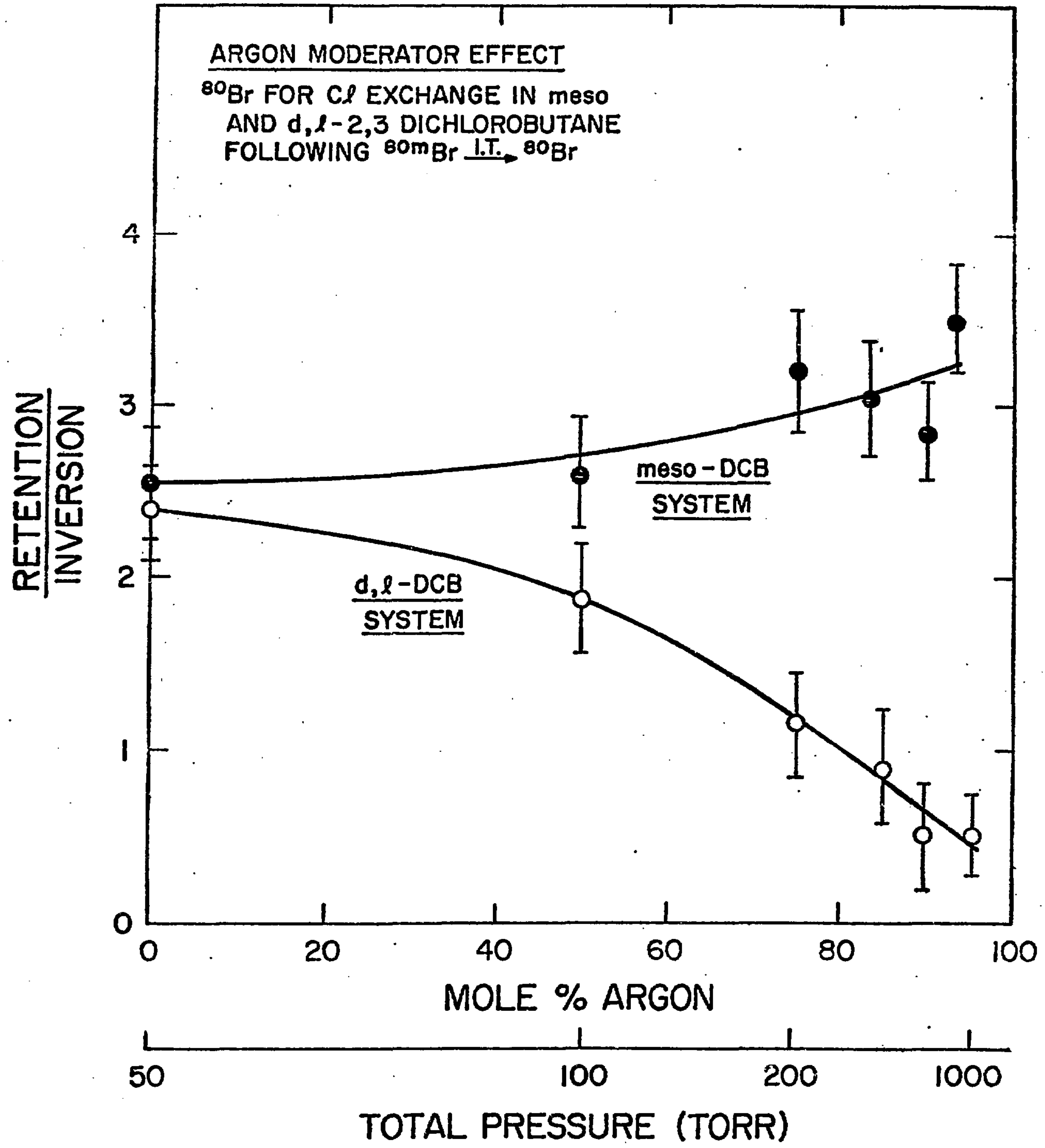

ARGON MODERATOR EFFECT
^{80}Br FOR Cℓ EXCHANGE IN meso AND d,ℓ-2,3 DICHLOROBUTANE FOLLOWING ^{80m}Br $\xrightarrow{I.T.}$ ^{80}Br
RETENTION / INVERSION
0
1
2
3
4
meso-DCB SYSTEM
d,ℓ-DCB SYSTEM
0
20
40
60
80
100
MOLE % ARGON
50
100
200
1000
TOTAL PRESSURE (TORR)

Fig. 2

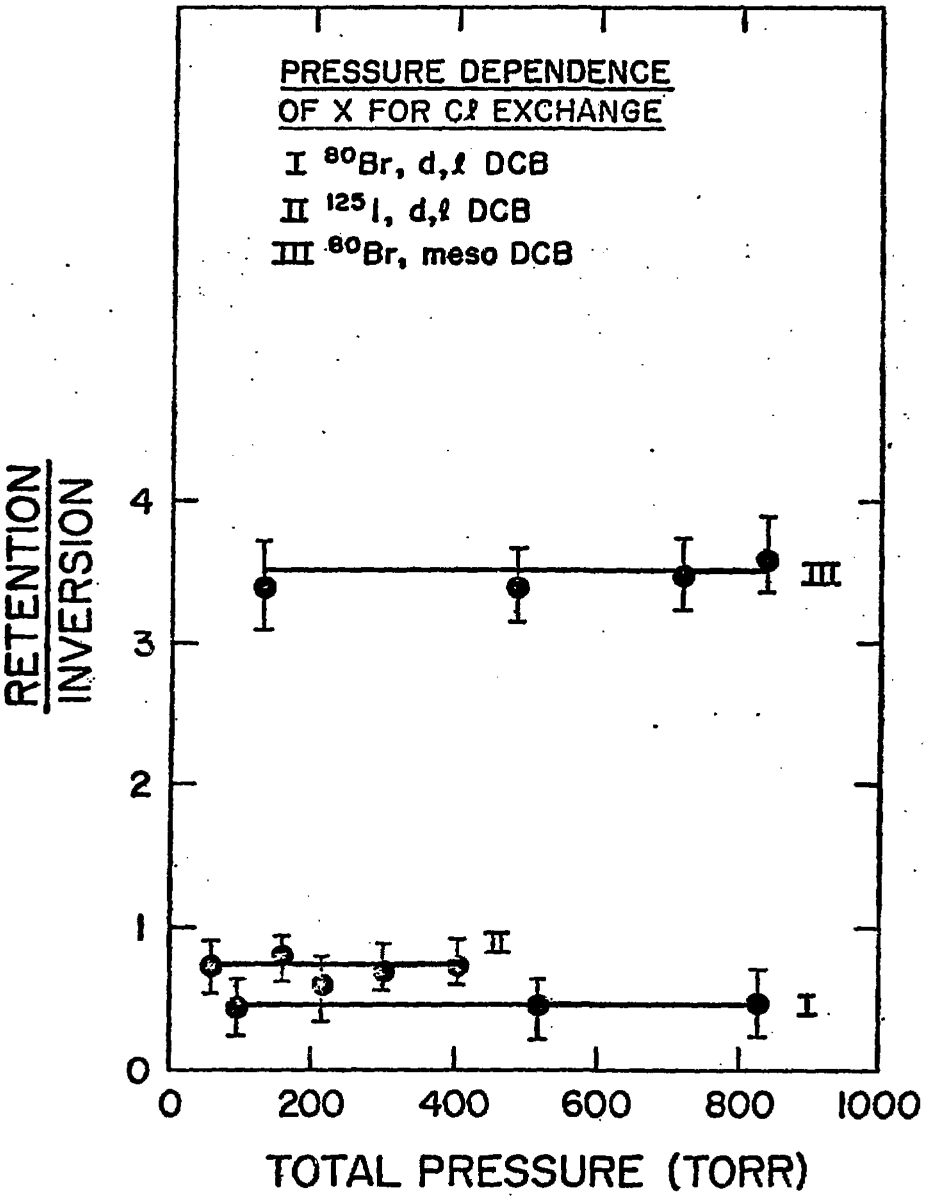
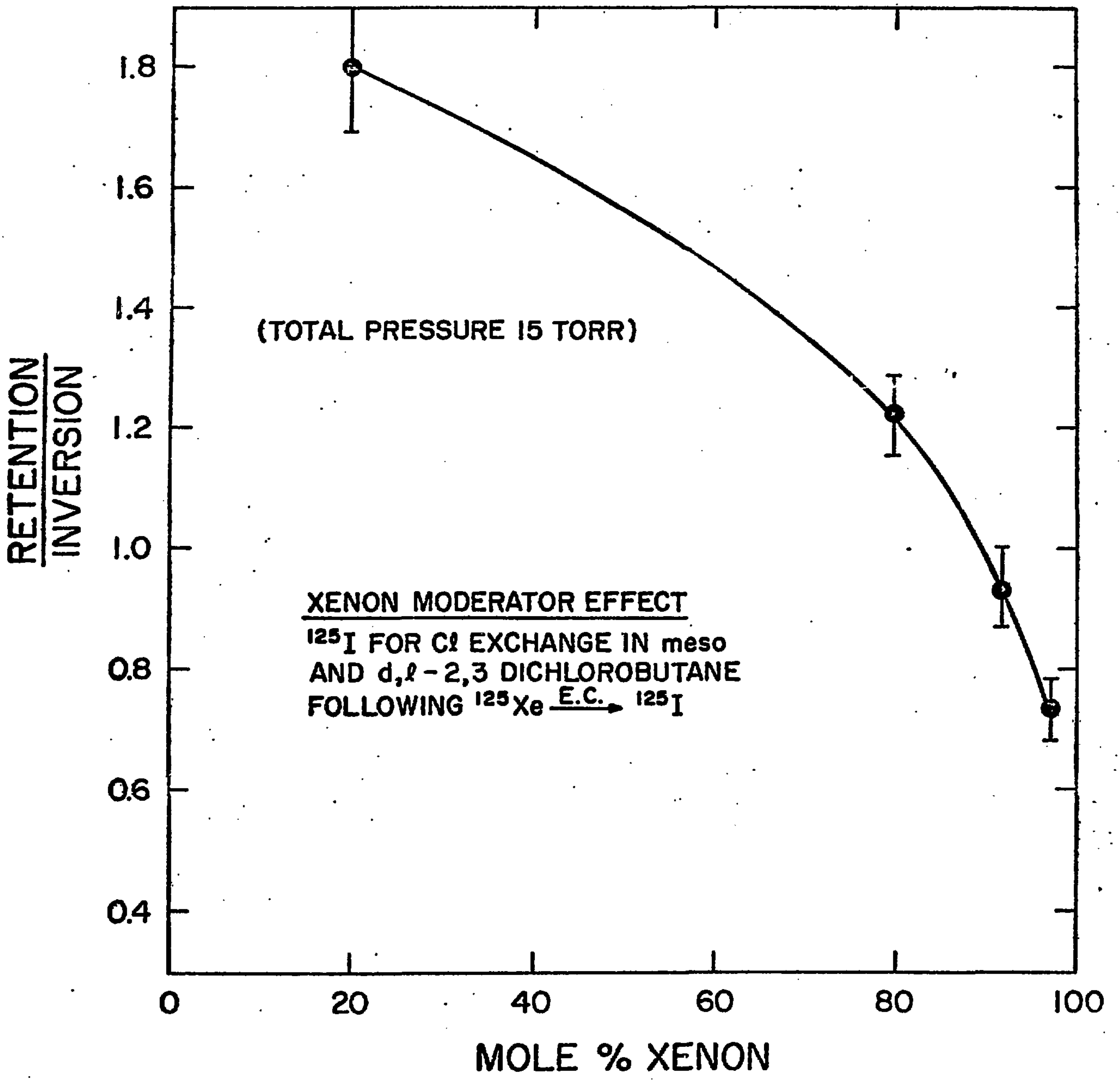
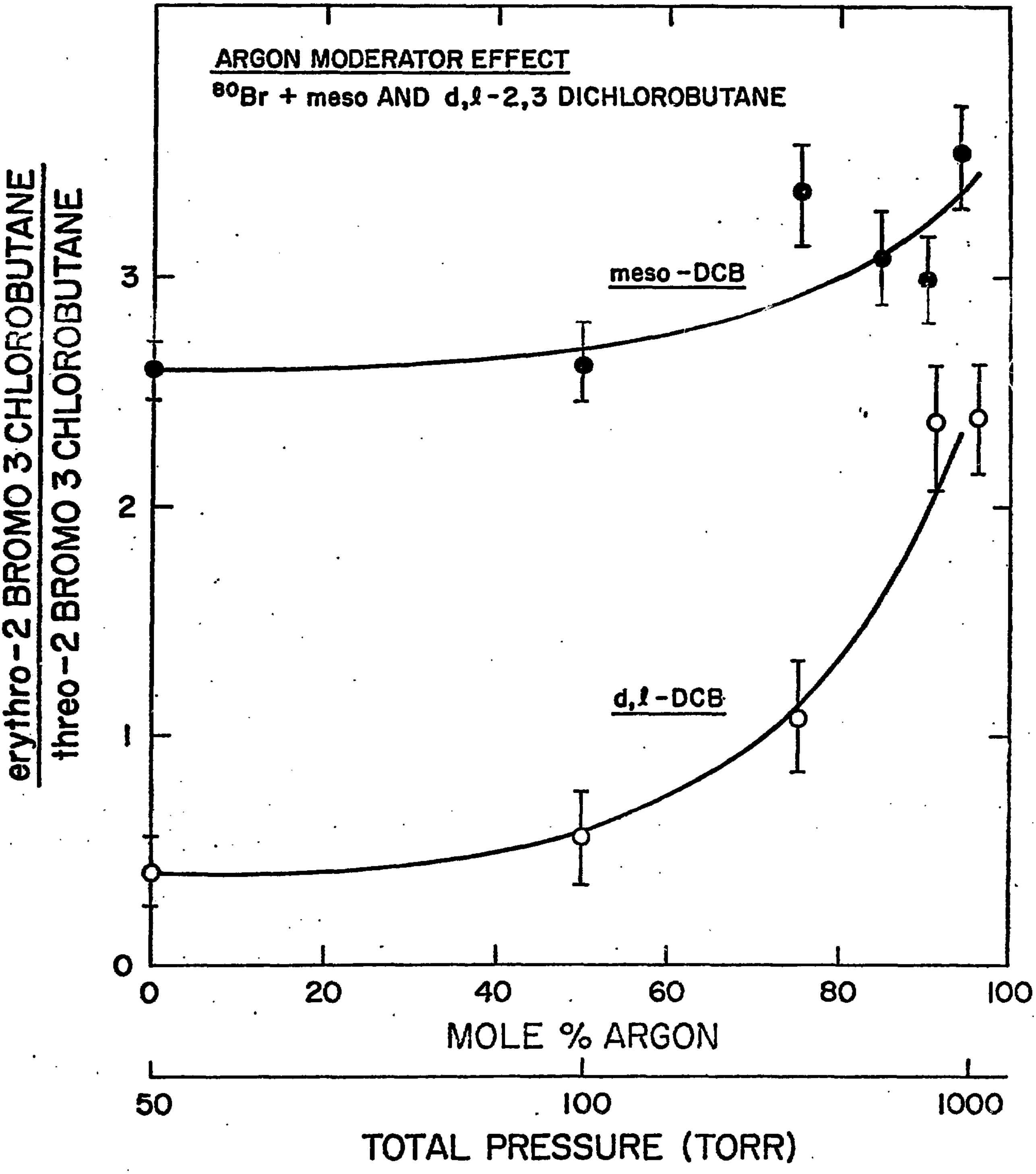

PRESSURE DEPENDENCE
OF X FOR Cℓ EXCHANGE
I ^{80}Br, d,ℓ DCB
II ^{125}I, d,ℓ DCB
III ^{80}Br, meso DCB
RETENTION / INVERSION
0
1
2
3
4
0
200
400
600
800
1000
TOTAL PRESSURE (TORR)
I
II
III

Fig. 3


1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
RETENTION / INVERSION
0
20
40
60
80
100
MOLE % XENON
(TOTAL PRESSURE 15 TORR)
XENON MODERATOR EFFECT
125I FOR Cl EXCHANGE IN meso
AND d,l-2,3 DICHLOROBUTANE
FOLLOWING 125Xe E.C. → 125I

4


ARGON MODERATOR EFFECT
^{80}Br + meso AND d,ℓ-2,3 DICHLOROBUTANE
meso-DCB
d,ℓ-DCB
erythro-2 BROMO 3 CHLOROBUTANE / threo-2 BROMO 3 CHLOROBUTANE
0
1
2
3
0
20
40
60
80
100
MOLE % ARGON
50
100
1000
TOTAL PRESSURE (TORR)