

Reactions of Recoil Generated Chlorine-38 Atoms with 2,3-Dichlorohexafluoro-2-butene. Cis/Trans Isomerization Accompanying Chlorine for Chlorine Replacement

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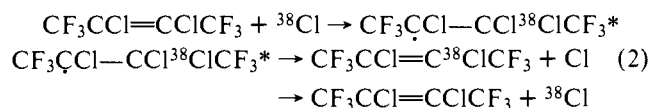
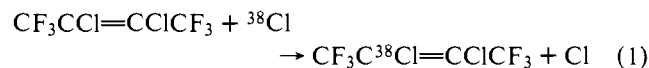
Abstract: Gas-phase reactions of nuclear recoil generated chlorine-38 atoms with 2,3-dichlorohexafluoro-2-butene (2,3-DCHF2B) result predominantly in chlorine for chlorine substitution. The reaction proceeds with geometrical isomerization, and the resulting cis-trans branching ratios are dependent on the isomeric identity of the reactant and the concentration of inert diluent present. Mechanistic features responsible for the observed behavior are discussed in terms of both a thermal or near-thermal reaction path and a concurrent high-energy process which preferentially forms trans product from both cis and trans reactants. The rate for addition of near-thermal chlorine atoms to 2,3-DCHF2B relative to addition to ethylene was found to be ~ 0.018 .

Introduction

The study of geometrical^{1,2} and optical³⁻⁶ isomerization accompanying recoil produced atom reactions with isomeric reactants can provide important insight into the energetics and mechanisms of such reactions. In general, gas-phase results have indicated that hot reaction processes proceed via a direct replacement with retention of configuration or structure.⁶ Low-energy and thermal reactions occur via abstraction or addition, the latter with accompanying rotation and cis-trans isomerization in competition with elimination.

Condensed-phase reactions with optically active reactants^{3,4} tend to be considerably more complex owing to the proximity of the solvent cage around the reaction site. Quantitative correlations in these systems have only recently been determined and suggest that the dielectric behavior of the solvent plays an important role in determining the detailed reaction path.³ Geometrical isomerization has also been studied in both liquid and solid phases for chlorine atom replacement reactions in 1,2-dichloroethylene² with results showing preferential retention of configuration but to a smaller extent than that observed for direct replacement in the gas phase.

Here we report results characterizing the gas-phase reactions of recoil generated chlorine atoms with 2,3-dichlorohexafluoro-2-butene (2,3-DCHF2B). Reaction proceeds primarily with chlorine atom replacement to yield radioactively labeled parent and may occur either directly as in eq 1 or via an excited radical intermediate as in eq 2.



At least part of the reaction is accompanied by cis-trans geometrical isomerization which is highly dependent on the isomeric identity of the reactant. The results are not consistent, however, with a simple mechanism based on a combination of low-energy thermally equilibrated reactions and high-energy replacement reactions with retention of configuration. The rate for chlorine atom addition to 2,3-DCHF2B relative to that with ethylene is also reported.

Experimental Section

Chlorine-38 atoms were generated via the $^{37}\text{Cl}(n,\gamma)^{38}\text{Cl}$ nuclear recoil reaction in the dry well of the ^{252}Cf source at the University of

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Utah.^{7a} Irradiations were performed for 20-30 min at ambient temperature in a thermal neutron flux of 5×10^7 n/cm²-s and a fast neutron flux of 2×10^7 n/cm²-s.

The maximum translational energy for the recoiling ^{38}Cl atom formed via this nuclear reaction is 528 eV. The mean translational energy calculated by us is 294 eV based upon the prompt γ -ray emission spectrum.^{7c} Failure to bond rupture is expected to be negligible based on the recoil energy distribution and thus essentially all of the labeled parent derives from chlorine atom reactions.

Radiation damage resulting primarily from γ radiolysis which is associated with this source was determined to be less than 0.001 eV/molecule as measured by an acetylene-to-benzene chemical dosimeter.⁸ The only other nuclear reactions observable under the irradiation conditions employed were the (n, γ) and (n,p) recoil processes with iodine when added and chlorine, respectively. Both contributions exhibited negligible radioactivity owing to the low concentration of iodine present and the short irradiation times employed. Potential products containing these isotopes of iodine and sulfur were easily distinguished by the gas chromatographic procedure used in the analysis.

Sample preparation and handling were by conventional high-vacuum techniques. Quartz reaction vessels (90 mL) contained gaseous mixtures of 2,3-DCHF2B reactant and CF_2Cl_2 which served both as a moderator and as a naturally abundant source of chlorine for the nuclear reaction. In some samples, C_2H_4 and I_2 at its ambient temperature vapor pressure were added as a scavenger for low-energy chlorine atoms.^{7a}

Phillips Research Grade ethylene and Matheson CF_2Cl_2 were used directly from lecture bottles without further purification after gas chromatography and mass spectroscopy indicated purities greater than 99.9%. The 2,3-dichlorohexafluoro-2-butene obtained from PCR, Inc., was a mixture of both cis and trans isomers with a reported purity of 85-90%. Separation of the isomeric forms was accomplished gas chromatographically on a 20-ft column of 20% SF-96 silicone oil on Chromosorb P support. Individual isomers were collected in Pyrex storage containers at liquid nitrogen temperature and the helium carrier gas was removed by degassing with repeated freeze-thaw cycles under high vacuum. Final purities of the isomers were determined gas chromatographically to be greater than 99.5% with the remaining impurity exclusively the other isomer. Identities of the two isomers were established by ^{19}F NMR through comparison with published spectral and chemical shift data.⁹

Sample handling and analysis techniques were identical with those described previously.^{7a,b} Geometrical isomerization was monitored radiogas chromatographically by comparing absolute yields of the ^{38}Cl -labeled cis and trans isomers of 2,3-DCHF2B. The total number of labeled molecules in a typical experiment was 6×10^7 so that the experiment is conducted without macroscopically perturbing the reaction mixture. Doubly labeled products are avoided as is the interaction of any two primary reaction products using this technique. Unlabeled carrier quantities of both isomeric forms were added to irradiated samples prior to chromatographic analysis to ensure complete product elution. Other chromatographic columns used in

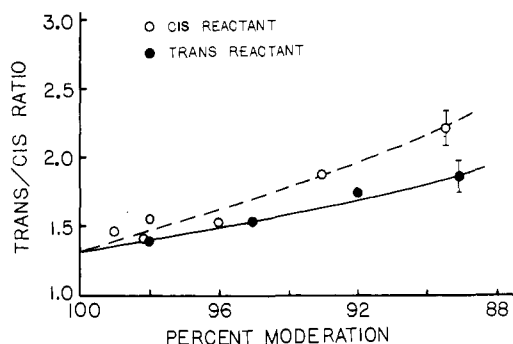


Figure 1. Absolute yield ratios of ^{38}Cl -labeled 2,3-DCHF2B as a function of moderation with CF_2Cl_2 at 1000 Torr total pressure. ●, unlabeled trans reactant; ○, unlabeled cis reactant.

determining relative rates of chlorine atom addition were a 5-ft, 5% SF-96 silicone oil column and a 15-ft, 20% hexamethylphosphoramide column.

Results

The systematics of the 2,3-DCHF2B reaction with nuclear recoil generated ^{38}Cl atoms were investigated in detail since studies of hot and thermal reactions in this unsaturated perhalo system have not been previously reported. It was anticipated that 2,3-DCHF2B might be self scavenging via addition of low-energy ^{38}Cl atoms to the double bond as in reaction 2, and initial results confirmed that the dominant scavenger product was indeed labeled 2,3-DCHF2B. In reaction mixtures of 10% 2,3-DCHF2B and 90% CF_2Cl_2 at 1000 Torr total pressure, the summed yields of labeled *cis*- and *trans*-2,3-DCHF2B always accounted for $\geq 92\%$ of the absolute yield. No 1,1,2-trichlorotrifluoropropene was observed indicating that neither direct replacement of the CF_3 group nor elimination of CF_3 from an excited radical adduct occurred in competition with the chlorine for chlorine replacement reaction. The latter result indicates that any excess energy deposited in the radical was effective only in stimulating the lowest energy decomposition route. Competition between the perhalobutene scavenger and the CF_2Cl_2 source gas for low-energy ^{38}Cl appeared to be absent since the absolute yields of $\text{CF}_2\text{Cl}^{38}\text{Cl}$ and $\text{CFCl}_2^{38}\text{Cl}$ were $< 1\%$ and were approximately independent of composition changes over the range 1–12% 2,3-DCHF2B reactant. These products have been observed previously and are thought to arise from hot reactions with CF_2Cl_2 .^{7,10}

Iodine at its ambient temperature vapor pressure was inefficient in stabilizing radical intermediates formed by chlorine atom addition across the double bond in systems having a total pressure of 1000 Torr. Less than 0.05% iodotrichlorohexafluorobutane was formed in any sample containing I_2 scavenger. This indicates that decomposition by chlorine atom elimination was relatively fast competing with collisional stabilization in less than 10^{-10} s. Propagation of the radical by addition to 2,3-DCHF2B is not expected to compete on this time scale either and indeed no evidence for labeled dimer or polymer formation was ever observed. Because 2,3-DCHF2B reactant provided adequate scavenging in the two-component system it was used without addition of a secondary scavenger in all cases except where competitive reaction rates with ethylene were determined.

Geometrical Isomerization Accompanying ^{38}Cl Reaction with 2,3-DCHF2B. The thermal and photochemical isomerization characteristics of 2,3-DCHF2B have not been reported previously and little is known about the thermochemistry of the isomerization process. In this work the chromatographically separated *cis* and *trans* isomers showed no interconversion at ambient temperature in Pyrex or quartz storage containers exposed to room light over a period of 3 months and produced

Table I. Branching Ratios for ^{38}Cl Labeled *cis*- and *trans*-2,3-Dichlorohexafluoro-2-butene as a Function of Moderation with CF_2Cl_2

Unlabeled reactant	% CF_2Cl_2 moderator	% absolute yield		Trans/cis ratio labeled product
		<i>cis</i> -2,3-DCHF2B	<i>trans</i> -2,3-DCHF2B	
<i>cis</i> -2,3-DCHF-2B	99.0	39.3	58.4	1.49
	98.2	38.9	55.5	1.43
	98.0	36.4	56.4	1.55
	96.0	38.9	58.6	1.51
	93.1	34.0	63.3	1.86
	89.4	28.9	63.5	2.20
<i>trans</i> -2,3-DCHF2B	98.1	38.9	55.2	1.42
	95.0	37.8	57.5	1.52
	91.9	35.5	62.3	1.75
	89.0	32.7	61.6	1.88

less than 1% isomerization in 76 h at 150 °C. Neither background radiation from fluorescent room lighting nor exposure to ^{252}Cf fission radiation during the recoil experiment caused detectable isomerization. Thus no unusual procedures or corrections to the data were required for the study of recoil chlorine reactions with the isomeric reactants.

Initial results were obtained for the absolute yields of isomer products of the ^{38}Cl for Cl replacement reaction from both *cis*- and *trans*-2,3-DCHF2B as a function of moderation. The CF_2Cl_2 moderator concentration was varied over the range 89–99 mol % at a total pressure of 1000 Torr. Since increased moderation lowers the average energy for reaction in self-scavenging reactants, the experiment was designed to study the energy dependence of the isomerization process. Less dilute systems were not investigated at this total pressure in our ambient temperature irradiation station owing to the low equilibrium vapor pressure of the perhalobutene isomers.

The ratios of the absolute yields of *trans* to *cis* products as a function of dilution with CF_2Cl_2 over this range are shown in Figure 1 and the absolute yields for representative points on this curve are listed in Table I. In the limit of high moderation where the nuclear recoil reaction approaches a totally thermalized system, the *trans*/*cis* ratio of labeled products from either unlabeled reactant isomer extrapolates to a common value of ~ 1.3 . It is interesting to note that this value is within experimental error of the photostationary equilibrium value of 1.26 ± 0.07 determined by us for this molecule.¹¹

At lower moderator concentrations and corresponding higher average reaction energies, the *trans*/*cis* ratio becomes increasingly dependent on the identity of the reactant isomer. For either reactant, the *trans*/*cis* product ratio increases with increasing reaction energy with the ratio from *cis* reactant always larger than that from *trans* reactant.

The energy dependence of the isomerization reaction was further investigated by monitoring the effect of adding a second scavenger to the reactive system. The ethylene- I_2 scavenger was chosen for this investigation since it has been well characterized^{7,12,13} and reacts primarily with low-energy, near-thermal ^{38}Cl atoms.^{7a,14} The added ethylene is expected to compete with the perhalobutene for low-energy ^{38}Cl atoms, and by doing so reduce the fraction of labeled 2,3-DCHF2B formed at low reaction energies. Small quantities of the ethylene- I_2 scavenger, however, should only slightly perturb the overall energy distribution of the recoil chlorine atoms, and the probability of high-energy reaction between ^{38}Cl and 2,3-DCHF2B is expected to remain essentially the same with or without the additional scavenger. The yield of labeled perhalobutene product in the system with the ethylene- I_2 scavenger

Table II. Experimentally Determined Trans/Cis Product Branching Ratios for Labeled 2,3-Dichlorohexafluoro-2-butene as a Function of Ethylene Concentration at 96% Moderation with CF_2Cl_2

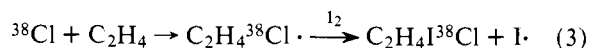
Unlabeled reactant	% ethylene	Trans/cis ratio labeled products
<i>cis</i> -2,3-DCHF2B	0	1.55
	0.10	2.08
	0.28	2.38
	0.60	2.30
<i>trans</i> -2,3-DCHF2B	0	1.51
	0.10	1.64
	0.28	1.95
	0.62	1.82

is thus expected to show additional weighting from high-energy reactions if indeed such reactions are important. As will be shown below, ethylene is approximately 114 times as efficient as 2,3-DCHF2B in scavenging near-thermal ^{38}Cl atoms which allows for competitive reaction at relatively low ethylene concentrations.

The competitive reaction with ethylene was investigated at a total pressure of 1000 Torr by varying the concentration of ethylene from 0.1% to 0.6% in a reaction system containing 4% 2,3-DCHF2B reactant, 96% CF_2Cl_2 source and moderator gas, and I_2 at its ambient temperature vapor pressure. The maximum value of 0.6% ethylene was chosen to maintain 25% of the total activity in the perhalobutene product and ensure adequate counting statistics. The mixture of the two competitive reactants produced only the two expected scavenger products, iodochloroethane and 2,3-DCHF2B. The resulting ratio of trans/cis labeled 2,3-DCHF2B product from each unlabeled parent is given in Table II and plotted in Figure 2 as a function of ethylene concentration.

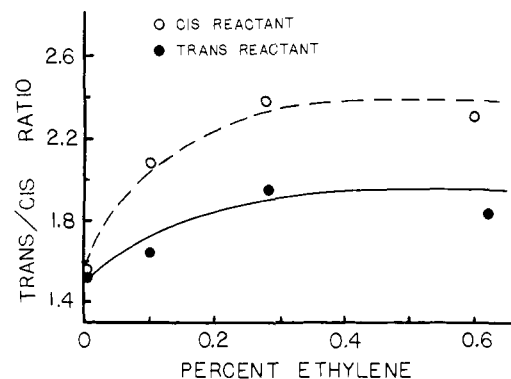
The results of the ethylene scavenger study again exhibit a dependence of the trans/cis branching ratios of labeled substitution product on the identity of the reactant. As the isomerization reaction of perhalobutene is weighted toward higher average energies by competitive ethylene scavenging, the trans/cis product ratio increases for either isomeric parent. As was seen in the moderation study of Figure 1, the *cis* reactant exhibits a higher trans/cis product ratio than the *trans* reactant. The product ratio does not extrapolate to the common low-energy value of 1.3 in the absence of ethylene since this study was carried out at a fixed moderation of 96%.

Relative Rates for Chlorine Atom Addition to 2,3-DCHF2B and Ethylene. The overall reactivity of chlorine atoms with 2,3-DCHF2B was measured relative to the addition reaction with ethylene. Relative rates were determined by varying the concentrations of the two reactants and monitoring the absolute yields of the resulting labeled products. As reported previously,^{7a} the low-energy reaction of ^{38}Cl with ethylene in the presence of I_2 at its ambient temperature vapor pressure proceeds primarily by the stepwise addition to form iodochloroethane product:



In all reactant mixtures of ethylene and 2,3-DCHF2B, the absolute yields of the two major products accounted for $\geq 95\%$ of the sample activity, and the two olefinic reactants showed no evidence of further reaction mechanisms involving both entities.

The relative rates of reaction for ^{38}Cl atoms with 2,3-DCHF2B and ethylene were determined in the presence of 90% CF_2Cl_2 and I_2 at its ambient temperature vapor pressure with a total system pressure of 1000 Torr. At 90% moderation it is anticipated that low-energy reaction processes should domi-

**Figure 2.** Dependence of the trans/cis branching ratio of labeled 2,3-dichlorohexafluoro-2-butene on ethylene scavenger concentration at 96% moderation with CF_2Cl_2 and 1000 Torr total pressure. ●, unlabeled *trans* reactant; ○, unlabeled *cis* reactant.**Table III.** Experimentally Determined Relative Reactivities of 2,3-Dichlorohexafluoro-2-butene and Ethylene with Chlorine-38 Atoms

Sample no.	Ratio of unlabeled reactant concn 2,3-DCHF2B/ ethylene	% absolute yields		Rel reactivities ethylene/ 2,3-DCHF2B
		$\text{C}_2\text{H}_4\text{I}^{38}\text{Cl}$	$\text{C}_4\text{F}_6\text{Cl}^{38}\text{Cl}$	
1	40.0	74.7	20.6	145
2	16.1	80.5	13.1	99
3	15.4	84.2	12.2	106
4	6.45	91.0	5.48	107
Average relative reactivity = 114 ± 20				

nate, although the distribution of reacting ^{38}Cl atoms is not expected to be fully thermalized. The absolute yields of the two primary addition products as a function of reactant concentration are shown in Table III. From this data the relative reactivities were determined per unit of reactant present and are listed. The average of these ratios was calculated to be $R_{\text{C}_2\text{H}_4}/R_{2,3\text{-DCHF}_2\text{B}} = 114 \pm 20$. Since the probability of elimination of a labeled chlorine atom is about the same as that for an unlabeled chlorine from an intermediate perhalobutane radical as in reaction 2, the rate of chlorine addition to the butene is twice the value obtained by observing only the labeled products. Thus, the relative rate ratio for addition to the respective double bonds is calculated to be $k_{\text{C}_2\text{H}_4}/k_{2,3\text{-DCHF}_2\text{B}} \sim 57$.

Discussion

The energy dependence of the *cis/trans* isomerization reaction accompanying recoil halogen atom reactions with alkenes has been interpreted previously in terms of a combination of low-energy and high-energy mechanisms.^{1,2} The low-energy reaction is postulated to be addition to the double bond followed by subsequent elimination from the intermediate radical. This establishes an equilibrium *trans/cis* labeled product ratio for the fraction of product formed by low-energy atoms. The concurrent high-energy mechanism is thought to be direct replacement which proceeds without isomerization. With 2,3-DCHF2B a dual reaction mechanism of this nature cannot completely account for the observed behavior. The 2,3-DCHF2B reactant exhibits an increasing preference for isomerization to the *trans* isomer from either parent as the average reaction energy is increased. Thus, the *cis* isomer shows increasing preference for inversion rather than retention of configuration at high energies. Therefore while a low-energy addition reaction with essentially free rotation in the radical

appears to occur, a parallel higher energy reaction also preferentially produces trans isomer which is postulated to be thermodynamically more stable than the cis isomer.

Low-Energy Addition-Elimination Processes. At the limit of infinite moderation, the nuclear recoil system must be characterized totally by low-energy reactions. In the two-component system of CF_2Cl_2 source gas and 2,3-DCHF2B reactant, the trans/cis ratio of labeled product from either reactant isomer is seen in Figure 1 to extrapolate at the high moderation limit to a common value of 1.3. The mechanism of isomerization at these low energies is expected to proceed by the addition of chlorine atoms to the double bond of 2,3-DCHF2B to form an intermediate radical. Such addition reactions are exothermic by approximately 20 kcal/mol,¹⁵ and the resulting internal energy is expected to be randomized among internal degrees of freedom.¹⁶ The initial internal energy of ~ 20 kcal/mol is greater than the activation barrier of < 1 kcal/mol¹⁷ for internal rotation around the central carbon-carbon bond, and the radical intermediate is expected to rotate freely. Following rotation, subsequent elimination of chlorine is expected to produce an isomeric mixture of 2,3-DCHF2B products which favors the thermodynamically more stable form. The addition-elimination mechanism results in both labeled and unlabeled products, but the unlabeled yields of products are below the limits of detection by conventional techniques and represent an extremely small perturbation of the microscopic sample composition.

Based on the photochemical results, the trans isomer is about 140 cal/mol more stable than the cis isomer. The increased stability of the trans isomer probably derives from steric interaction of the CF_3 groups which have considerably larger van der Waals radii than the Cl atoms¹⁸ and thus prefer a trans orientation. The common trans/cis product ratio of 1.3 seen from recoil reaction with either parent isomer in the limit of high moderation is consistent with the thermochemical estimates and appears to indicate that the low-energy addition-elimination mechanism results in free internal rotation leading to an equilibrium cis-trans product mixture.

High-Energy Reactions. The cross section for the ^{38}Cl reaction with 2,3-DCHF2B also appears to extend to energies well above the thermal threshold for addition. At high energies, the trans/cis ratios of labeled products are dependent on the isomeric parent used as reactant with the ratio being greater for the cis than for the trans reactant. While excess translational excitation of the ^{38}Cl atom may drive secondary high-energy reaction channels, direct replacement without isomerization which was observed in previous studies with 1,2-dichloroethylene^{1,2} does not appear to be the dominant mechanism in 2,3-DCHF2B.

In the reaction studied here, replacement with net inversion occurs in the cis reactant at high energy while net retention of the trans configuration occurs in the trans reactant. Since the total trans yield is always greater than the total cis yield, the result cannot originate simply from a high-energy randomization of configurations. This is in contrast to the results observed for the chlorine atom replacement in 1,2-dichloroethylene. In that case the thermodynamically more stable cis isomer is always formed in greater yield than the trans isomer, although an enhanced yield of trans product from both cis and trans reactant is observed as the reaction energy is increased. This indicates that a larger contribution of randomized products to the overall yield occurs at higher energies. The data reported here suggest a mechanism in which chlorine replacement occurs directly at high energies via trajectories favoring backside attack at or near the site of a CF_3 group. Factors such as

electron density and electronegativity have previously been correlated with yields in recoil tritium replacement reactions^{19,20} and may very well play a role in recoil chlorine reactions as well. If the CF_3 group has a positive influence in determining the course of the hot replacement reaction the increased reactivity of the cis isomer can also be accounted for in that the two neighboring CF_3 groups in the cis isomer should be more effective in directing the attacking chlorine than the corresponding groups in the trans isomer.

Undoubtedly additional factors play a role in the detailed mechanisms of the higher energy reaction channels. In particular, the possibility of electronically excited states of reaction intermediates cannot be ignored. Although the initial ^{38}Cl atom has been characterized as a ground-state neutral atom in previous recoil experiments,²¹ it can carry a sizable amount of kinetic energy into a reaction. It is quite possible that the high-energy reaction produces an excited radical or diradical upon addition or direct replacement in 2,3-DCHF2B and that the eventual product distribution from such a high-energy process favors the trans isomer to a greater extent than is expected from the equilibrium properties.

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