is equivalent to changing the interfacial dipole. Change in the Fermi level of the metal is inconsistent with our parallel measurements of the optical properties of these metal films with changing ambients: Significant changes in the metal Fermi level would have caused large changes in the Drude tail of the dielectric functions of the metals. Such changes were not observed.

Contributions from hydrogen doping of semiconductors other than InP cannot be ruled out, as shown for example by the reversible hydrogen-induced trapping state that we have observed in CdS. However, the general mechanism, that bears on all contacts, is the change in the surface dipole component of the metal work function upon changing the ambient gas.

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# Stereochemical Consequences of Halogen-for-Halogen Substitutions in the Gas Phase

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The stereochemistry of translationally energetic fluorine-for-halogen and chlorine-for-halogen substitution was studied in gaseous 2(S)- and 2(R)-halopropionyl halides. While net inversion of configuration was observed for halogen using <sup>34m</sup>Cl as the displacing agent, predominant retention of configuration was found when <sup>18</sup>F was used as the displacing agent on the chiral centers of the 2-halopropionyl halides. The extent of inversion or retention in these energetic substitution reactions appears to be sensitive to the mass of the incoming atom, to steric hindrance to back-side attack, and to the nature of the halogen leaving group.

## Introduction

One of the mechanistically important questions in recoil atom chemistry concerns retention vs. inversion of configuration in homolytic substitution  $(S_{HH}2)$  of recoil atoms at sp<sup>3</sup>-hybridized carbon in the gas phase.

$$\mathbf{X}_i^* + \mathbf{R}\mathbf{X}_j \xrightarrow{\mathbf{X}_i \text{ for } \mathbf{X}_j} \mathbf{R}\mathbf{X}_i^* + \mathbf{X}_j$$

Resolution of this point can provide insight into the dynamics of hot-atom reactions.

All recoil tritium substitution reactions<sup>1-7</sup> regardless of substrate molecules studies, or phase, occur with predominant retention of configuration. On the other hand, recoil fluorine,<sup>8</sup> chlorine,<sup>4,9,10</sup> bromine,<sup>11,12</sup> and iodine<sup>12</sup> substitu-

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tion reactions in the gas phase with substrate molecules containing two asymmetric centers occur mainly with retention of configuration but can in certain cases show appreciable yields of the inverted product. In the condensed phase<sup>13-18</sup> the results are not that clear-cut, ranging from 75% retention of configuration for <sup>38</sup>Cl-for-chlorine substitution in neat dl-dichlorobutane<sup>13</sup> to around 50% for several other systems.

An advance in the mechanistic aspects of these substitution reactions was made by Stöcklin et al.<sup>4,13</sup> in their studies of recoil chlorine-for-chlorine substitution in liquid solutions of 2,3-dichlorobutane (DCB) and gas, highpressure, and condensed-phase 1,2-dichloro-1,2-difluoroethane (DCDFE). They suggested that halogen-forhalogen substitution may involve two reaction channels:

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(1) a direct front-side replacement by the recoil atom leading to retention of configuration, and (2) the formation of an excited reaction complex with a lifetime long enough for configuration change. Since these authors did not observe significant yields of the inversion product in lowand high-pressure DCDFE systems, they suggested that inversion results from the formation of a complex possessing large excitation energies, within the confines of liquid cage, subsequently allowing the necessary rearrangement leading to the inverted product.

In the stereochemical study involving high-energy halogen-for-halogen substitution in compounds with single chiral centers, Wolf et al.<sup>14</sup> studied energetic <sup>34m</sup>Cl and  $^{38}$ Cl-for-Cl substitution at the chiral centers of 2(S)- and 2(R)-chloropropionyl chloride. These experiments provided the first evidence that recoil chlorine can effect Walden inversion in the gas phase with greater than 80% of the enantiomers being observed. However, an almost 40% decrease in the extent of inversion of configuration was observed in <sup>35m</sup>Cl-for-Cl substitution with 2-chloro-4methylvaleryl chloride, suggesting that steric hindrance to back-side attack could be expected.

The presence of a Walden inversion mode in gas-phase  $S_{HH}2$  reactions was further tested by studying the hot-atom substitution reaction of  $^{34m}$ Cl-for-Cl with 2(S)- and 2-(R)-chloro-1-propanol at low pressures.<sup>19</sup> Net inversion of configuration was again found to be predominant. These results<sup>14,19</sup> suggested that not all hot-atom substitution reactions are fast and direct involving a front-side approach in accordance with the impact model,<sup>20-22</sup> but can occur from the back side of the molecule resulting in Walden inversion. In an attempt to gain more insight into the S<sub>HH</sub>2 reaction, the high-energy fluorine-for-halogen and chlorine-for-halogen substitution reactions at chiral centers were investigated with chiral 2-halopropionyl halides in the gas phase.

#### **Experimental Section**

The experimental techniques employed have been described by us previously.<sup>14,19</sup> The 2(S)- and 2(R)-fluoropropionic acids were prepared according to the methods described by Olah et al.<sup>23,24</sup> The method described by Fu et al.<sup>25</sup> was used to prepare (-)-2(S)- and (+)-2(R)chloropropionic acids and (-)-2(S)-bromopropionic acid. The 2-halopropionyl halide of the corresponding acid was prepared by mixing the acid with benzoyl fluoride, benzoyl chloride, or benzoyl bromide in a distillation apparatus in an oil bath previously heated to about 120 °C. The 2halopropionyl halide was distilled over as quickly as possible. The crude acid was then redistilled by using a fractional distillation column. The optical purities of the acyl halides were found to be greater than 90% in every case. Irradiations were carried out at the Brookhaven National Laboratory 60-in. cyclotron. For all <sup>34m</sup>Cl substitution studies with 2-halopropionyl halides a 20-MeV proton beam was used to produce <sup>34m</sup>Cl by the <sup>35</sup>Cl(p,pn)<sup>34m</sup>Cl reaction. For <sup>18</sup>F substitution reactions with 2-chloropropionyl chloride and 2-bromopropionyl bromide and systems containing neon additive, a 13-MeV deuteron

TABLE I: Yields of <sup>34</sup><sup>m</sup> Cl-for-F, <sup>34</sup><sup>m</sup> Cl-for-Cl, and <sup>34</sup><sup>m</sup> Cl-for-Br Substitution at the Asymmetric Carbon of (+)-2(S)-Halopropionyl Halides in the Gas Phase

enantiomer, %	press.,	absolute	retention,
	torr	yield, %	%
(+)-2(S)-CH <sub>3</sub> CHFCOF (+)-2(S)-CH <sub>3</sub> CHFOCl (+)-2(S)-CH <sub>3</sub> CHClCOF (+)-2(S)-CH <sub>3</sub> CHClCOCl (+)-2(S)-CH <sub>2</sub> CHBrCOBr	500 500 500 400 500	$\begin{array}{c} 0.8 \pm 0.1 \\ 1.2 \pm 0.2 \\ 1.3 \pm 0.1 \\ 1.3 \pm 0.1 \\ 2.3 \pm 0.3 \end{array}$	$\begin{array}{c} 29 \pm 3 \\ 27 \pm 1 \\ 23 \pm 2 \\ 19 \pm 2 \\ 22 \pm 3 \end{array}$

beam was employed producing <sup>18</sup>F by the <sup>20</sup>Ne(d, $\alpha$ )<sup>18</sup>F reaction. A 1-5 mol % Ne concentration in the reaction vessels was used for the 2-chloropropionyl chloride and 2-bromopropionyl bromide systems. For <sup>18</sup>F substitution systems, <sup>18</sup>F was produced by the <sup>19</sup>F(p,pn)<sup>18</sup>F reactions employing a 20-MeV proton beam. The samples received an average irradiation of 60 A s. Thus, the displacing atom was prepared in situ in the gas. After irradiation the acyl halides were allowed to react with 2(S)-value methyl ester. The resulting diastereomers were separated by GLPC using a 1/4 in.  $\times$  25 ft glass column packed with 17% Carbowax 20 M on Anakrom Q 80/100 mesh at 175 °C with a helium flow rate of 80 mL/min. The (S,R) and (S,S) diastereomers of N-(2-fluoropropionyl)-(S)-valine methyl ester eluted at 20 and 30 min, respectively, while the (S,R) and (S,S) diastereomers of N-(2-chloropropionyl)-(S)-valine methyl ester gave a retention time of 74 and 95 min, respectively.

Absolute yields for the <sup>18</sup>F and <sup>34m</sup>Cl substitution reactions at the asymmetric carbon of the acyl halides were also determined. The experimental techniques used to determine the absolute yields for <sup>18</sup>F and <sup>34m</sup>Cl substitutions were similar to the ones described by us.<sup>14b</sup> The total induced <sup>18</sup>F activity in the samples was monitored by placing a circular 2-mil Kapton Type H foil (a polyamide film manufactured by E. I. du Pont de Nemours and Co.) at the front and back windows of the reaction vessel during sample irradiation. The proton flux through the sample was calculated by measuring the <sup>11</sup>C activities (at EOB) in the two 2-mil Kapton foils. The total induced <sup>18</sup>F activity was then calculated from the proton flux through the sample estimated by the foil techniques.

Control experiments similar to the ones previously reported<sup>14b,19</sup> in which derivatization was run in the presence of externally generated <sup>34m</sup>Cl or <sup>18</sup>F in admixture with the substrate were carried out. Results of these control experiments showed that isotopic exchange reactions at the chiral center were not significant under the conditions employed for the derivatization of the diastereomers.

### Results

The absolute yields and percent retention of configuration are given in Table I for the various systems in the gas-phase <sup>34m</sup>Cl-for-F, <sup>34m</sup>Cl-for-Cl, and <sup>34m</sup>Čl-for-Br substitution at the asymmetric carbon atoms of (+)-2(S)halopropionyl halides. The percent inversion of configuration yields is, of course, 100 - % retention yield. These gas-phase results are clearly in the same direction as our previous results<sup>14,19</sup> for chloropropionyl chloride and 2chloro-1-propanol where predominant inversion was observed. The data in Table I show a decrease in retention proceeding from CH<sub>3</sub>CHFCOX and CH<sub>3</sub>CHClCOX leveling off for CH<sub>3</sub>CHBrCOBr. The absolute percent yield for the <sup>34m</sup>Cl-for-Br substitution  $(2.3 \pm 0.3\%)$  is greater than that of the  $^{34m}$ Cl-for-F substitution (0.8 ± 0.1%).

Presented in Table II are the absolute yields and percent retentions of optical activity at various system pressures for the gas-phase <sup>18</sup>F-for-F, <sup>18</sup>F-for-Cl, and <sup>18</sup>F-for-Br

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TABLE II: Yields of <sup>18</sup>F-for-F, <sup>18</sup>F-for-Cl, and <sup>18</sup>F-for-Br Substitution at the Asymmetric Carbon of (+)-2(S)-and (-)-2(R)-Halopropionyl Halides in the Gas Phase

enantiomer, %	press., torr	[neon], mol %	absolute yield, %	retention, %
$(+)-2(S)-CH_{3}CHFCOF^{a}$	300		$0.8 \pm 0.1$	69 ± 2
(-)-1(R)-CH <sub>3</sub> CHFCOF <sup>a</sup>	300		$1.0 \pm 0.2$	$72 \pm 3$
$(+)-2(S)-CH_{3}CHFCOF^{a}$	500		$1.6 \pm 0.1$	$71 \pm 3$
$(+) \cdot 2(S) \cdot CH_{3}CHFCOF^{b}$	500	<b>34</b>	$1.0 \pm 0.1$	
$(+)-2(S)-CH_{C}CHFCOF^{b}$	500	55	$0.33 \pm 0.04$	
$(+) - 2(S) - CH_3 CHFCOF^{b}$	500	67	$0.15 \pm 0.02$	$67 \pm 4$
$(+) - 2(S) - CH_{CHFCOF^{b}}$	500	80	$0.08 \pm 0.02$	$62 \pm 4$
$(+) \cdot 2(S) \cdot CH_{3} CHFCOF^{b}$	500	85	$0.06 \pm 0.01$	$61 \pm 4$
$(-)^{2} (R)^{2} CH^{2} CHFCOF^{a}$	500		$1.3 \pm 0.2$	$73 \pm 2$
(-)-2(R)-CH,CHFCOF <sup>a</sup>	750		$1.7 \pm 0.$	$70 \pm 2$
(+)-2 $(S)$ -CH, CHFCOCl <sup>a</sup>	500		$0.8 \pm 0.2$	69 ± 1
$(+) \cdot 2(S) \cdot CH \cdot CHClCOF^{a}$	500		$1.0 \pm 0.1$	$64 \pm 2$
$(+) - 2(S) - CH_{2}CHClCOCl^{c}$	500		$1.1 \pm 0.1$	65 ± 2
$(+)-2(S)-CH_{3}CHBrCOBr^{c}$	500		$2.0 \pm 0.4$	61 ± 2

<sup>a</sup> The displacing fluorine atom was generated in situ by the <sup>19</sup>F(p,pn)<sup>18</sup>F reaction. <sup>b</sup> The fluorine atom was generated by the <sup>20</sup>Ne( $d,\alpha$ )<sup>18</sup>F reaction. <sup>c</sup> The fluorine atom was generated by the <sup>20</sup>Ne( $d,\alpha$ )<sup>18</sup>F reaction employing a 1-5 mol % Ne concentration.

substitution at the asymmetric carbon atoms of (+)-2(S)and (-)-2(R)-halopropionyl halides. The level of retention for the R and S isomers (where both were measured) of the 2-halopropionyl halides were identical within experimental error. Unlike the recoil <sup>34m</sup>Cl substitutions, where net inversion of optical configuration was found, the results for the <sup>18</sup>F reactions show predominant retention of configuration similar to what was observed in <sup>18</sup>F reactions in meso- and dl-(CHFCl)<sub>2</sub>.<sup>8</sup> The absolute yield of <sup>18</sup>F-for-F substitution in (-)-2(R)-CH<sub>3</sub>CHFCOF decreases with increasing mole percent neon, suggesting that <sup>18</sup>F-for-F substitution at the chiral center of (-)-2(R)-CH<sub>3</sub>CHFCOF involves high-energy (hot) fluorine atoms. There does not appear to be an appreciable change in percent retention with decreasing mole percent neon. The data of Table II indicate a trend in decreasing retention in going from the neat 2-fluoropropionyl halides to the 2-chloropropionyl halide and 2-bromopropionyl bromide. In addition, the yield pattern in the neat system shows <sup>18</sup>F-for-Br substitution  $(2.0 \pm 0.4\%)$  to be greater than that for the <sup>18</sup>F-for-F substitution  $(0.8 \pm 0.1\%)$ .

#### Discussion

It is generally recognized<sup>20</sup> that recoil tritium, fluorine, and chlorine produced by nuclear transformations should react as neutral atoms in a halocarbon environment whose ionization potential is lower than the first ionization potential of the recoil atom. Ionic states of these recoil species should not play a significant role in the substitution process. In all previous studies of recoil fluorine-forfluorine and recoil chlorine-for-chlorine sbustitution where rare gas moderators were employed, the recoil reactivity was found to be the result of the initially high translational energy that the recoil atom acquires by virtue of the nuclear transformation. This is consistent with  $evidence^{26}$ that no thermoneutral homolytic bimolecular substitution  $(S_{H}2)$  reactions at unstrained sp<sup>3</sup>-hybridized carbon atoms have been observed. However, recently Iyer and Rowland,<sup>27,28</sup> employing moderated recoils, observed thermal (exothermic) F/X atomic substitution reactions with methyl halides (X = Cl, Br, I). In order to test for a possible thermal fluorine-for-fluorine substitution reaction the effect of neon moderators was studied on the absolute yield for the <sup>18</sup>F-for-F substitution at the asymmetric

carbon of (+)-2(S)-CH<sub>3</sub>CHFCOF. As expected for the thermoneutral substitution and as seen in Table II, the absolute yield of the labeled substitution product is quite small,  $0.03 \pm 0.01\%$  at 85 mol % Ne, as compared to an unmoderated yield of  $1.6 \pm 0.1\%$ . For this system it would appear that any thermal contribution is quite small; however, it does not rule out small thermal contributions for substitution reactions for chlorine or bromine atoms at the chiral center.

As can be seen in Tables I and II, the recoil halogenfor-halogen substitution yields of <sup>18</sup>F and <sup>34m</sup>Cl at the chiral centers of the 2-halopropionyl halides do not result in either complete retention or complete inversion of configuration. A complete (100%) retention or inversion of configuration for S<sub>HH</sub>2 reactions has not been observed in any system. However, recoil tritium substitutions approach 100% retention.<sup>1-7</sup> Retention of configuration for <sup>18</sup>F is 60–70% while "retention" of configuration for <sup>34m</sup>Cl is 20–30% (see Tables I and II). Thus, the degree of inversion increases with the mass of the incoming atom.

Stöcklin et al.4,13 originally speculated that product formation involved excessive excitation energy and this reaction mode would become significant primarily in the condensed phase where stabilization of a complex could occur. Thus, these authors suggested the possibility of two reaction channels for hot halogen substitution (front-side attack or complex formation). Our observations showing that <sup>34m</sup>Cl-for-halogen substitution in the gas phase resulting in an inversion of configuration involves minimal excitation energies. A two-reaction-channel model (front-side vs. back-side attack) has been suggested by the computer simulation trajectory studies of the  $T + CH_4$ hot-atom reactions described by Bunker et al.<sup>29-31</sup> They predict some substitutions in methane as proceeding with inversion, the inversion mode predominating at relatively low energy and retention at higher energies.

If two reaction channels are indeed operative in recoil fluorine or recoil chlorine substitution reactions, one involving a front-side attack of the hot atom on the substrate molecule, resulting in retention of configuration, and the other a back-side approach, proceeding with inversion of configuration, it may be possible to observe variations in substitution yields with substrate molecule parameters consistent with a two-reaction-channel model. It has been

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suggested that recoil atom substitution with retention of configuration, according to the impact and inertial models, $2^{2-22}$  extended32,33 to recoil fluorine and chlorine, (1) is not accompanied by excessive motion among the substituent groups and proceeds by a frontal attack whose duration is the same order of time required for the atom to pass the molecule, comparable to a period of bond vibration, (2) is insensitive to bond energies, and (3) is dependent solely upon the site and direction of collision. There is some question about the reactions of recoil atoms being insensitive to bond energy. Rowland et al.,<sup>34</sup> in their study of the roles of chemical factors in controlling yields of energetic tritium atoms, found that a major factor in controlling the variations in yield with the substituent X in the T-for-X substitution is the bond dissociation energy of the C-X bond. Bunker et al.<sup>35</sup> suggest that recoil atom reactions, even well above thermal energies, may be quite sensitive to the bond dissociation energy of this reacting bond. Unlike recoil atom reactions with retention of configuration, explained by the impact and inertial models,  $^{20\mathchar`-22,32,33}$  concepts or models for  $S_{\rm HH}2$  reactions with inversion of configuration have not yet been developed.

It is proposed that  $S_{HH}^2$  reactions at sp<sup>3</sup>-hybridized carbon involving monovalent recoil atoms can occur by either of two reaction channels, one with retention of configuration and the other with inversion of configuration. The relative extent of these channels is dependent on the mass of the recoil atom, steric hindrance to back-side attack at the sp<sup>3</sup>-hybridized carbon, the energy of the recoil atom at the time of the reactive collision, and the nature of the halogen leaving group. In addition, other factors such as those proposed by Rowland<sup>34</sup> for energetic tritium atoms may have importance in the substitution process, namely, bond energy, electronegativity, and electron density. A reactive collision with substitution with retention of configuration involves a frontal attack at the bonded halogen atom at wider angles than that for abstraction in which the time taken for bond formation is less than the time reequired for the necessary motions of the substituent groups during the inversion mode. Thus, the energy imparted during a reactive collision leading to retention is localized at the site of impact and not distributed over neighboring bonds. A reactive collision with inversion of configuration involves back-side attack in which the time taken for product formation is long enought to allow for the necessary motions of the substituents. In addition, an inverting substitution reaction is sensitive to steric obstruction to back-side attack and to the nature of the leaving halogen, i.e., its mass, size, polarizability, etc. The most critical factor controlling the degree of inversion is the mass of the incoming atom. In addition, steric hindrance plays a significant role in these substitution reactions. For 10-2-eV T atoms, the energy range for probable reactive collisions, collision times range from  $8 \times 10^{-15}$  to  $2 \times 10^{-14}$  s, shorter than all carbon-halogen and carbonoxygen bond vibration times but comparable to that of the carbon-hydrogen bond. It is apparent why recoil tritium substitution reactions proceed predominantly with retention. For 10-2-eV <sup>18</sup>F and <sup>34m</sup>Cl atoms, collision times range from  $2 \times 10^{-14}$  to  $4 \times 10^{-14}$  s and from  $3 \times 10^{-14}$  to  $6 \times 10^{-14}$  s, respectively. These collision times, while longer than vibration times of the carbon-hydrogen and carbon-oxygen bonds, are of the same order as that of the carbon-halogen bonds. Unlike recoil fluorine-for-halogen substitution reactions at the chiral centers of 2-halopropionyl halides, which occur with net retention of configuration, all recoil chlorine-for-chlorine substitution reactions occurred with net inversion of configuration. However, for recoil chlorine-for-chlorine substitution in gaseous 2-chloro-4-methylvaleryl chloride, steric hindrance to back-side attack results in slight favoring of the retention mode. Regardless of whether the recoil halogen substitution reaction proceeds with retention or inversion of configuration, the absolute substitution yields (see Tables I and II) are greatest for <sup>34m</sup>Cl-for-Br and <sup>18</sup>F-for-Br subsittution and lowest for <sup>34m</sup>Cl-for-F and <sup>18</sup>F-for-F substitution.

Inspection of the substitution data of Tables I and II suggests interesting trends in percent retention for <sup>18</sup>Ffor-halogen substitution and percent retention for <sup>34m</sup>Clfor-halogen substitution with 2-halopropionyl halide. For <sup>18</sup>F substitution the percent retention appears to decrease in the following order of leaving groups: fluorine, chlorine, and bromine. For <sup>34m</sup>Cl substitution the percent retention also decreases going from fluorine to chlorine with bromine substitutions being approximately equal to chlorine substitutions. The decrease in percent retention or, more importantly, the increase in percent inversion for <sup>18</sup>F and <sup>34m</sup>Cl as the leaving group goes from fluorine to chlorine to bromine may suggest possible sensitivity to polarizability electronegativity, size, and mass of the leaving atom. However, our present experiment cannot distinguish the relative importance of these factors. In conclusion, it appears that S<sub>HH</sub>2 reactions in the gas phase can occur by both front-side and back-side attack, their relative importance determined by the mass of the recoil atom, steric hindrance, and the nature of the leaving group in the substitution process, with the mass of the incoming atom being the predominant factor.

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**Registry No.** (+)-(*S*)-CH<sub>3</sub>CHFCOF, 87337-49-3; (-)-(*R*)-CH<sub>3</sub>CHFCOF, 87337-50-6; (+)-(*S*)-CH<sub>3</sub>CHFCOCl, 87337-51-7; (+)-(*S*)-CH<sub>3</sub>CHClCOF, 87337-52-8; (+)-(*S*)-CH<sub>3</sub>CHClCOCl, 70110-24-6; (+)-(*S*)-CH<sub>3</sub>CHBrCOBr, 87337-53-9; <sup>18</sup>F, 13981-56-1; <sup>34</sup>Cl, 13981-24-3.