

Figure 1. Shifts of the methylene (a) and carboxymethylene (b) protons of EDTA as a function of the Ru(bpy)<sub>3</sub><sup>2+</sup>:EDTA mole ratio (0.1 M EDTA and 0-0.2 M [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>).

M EDTA (>90% of the complex is present as the ion pair) are within experimental error of those of the free complex. Resonance-enhanced Raman spectra, which are sensitive to more subtle structural and/or electronic changes on the bipyridine periphery that might arise from an interaction with  $EDTA^{2-}$ , are equivalent to spectra of the free complex. With 457.9-nm excitation, resonance Raman spectra of Ru(bpy)<sub>3</sub><sup>2+</sup> above 1000 cm<sup>-1</sup> exhibit seven bipyridine modes.<sup>12</sup> In the presence of 0.1 M EDTA<sup>2-</sup>, the spectra of 0.1 and 0.01 M Ru(bpy)<sub>3</sub><sup>2+</sup> solutions are within experimental error in peak position,  $\pm 1$  cm<sup>-1</sup>, and relative intensity,  $\pm 10\%$ , of the spectra of the free complex. Emission lifetime measurements with deaerated solutions containing  $10^{-4}$  M Ru(bpy)<sub>3</sub><sup>2+</sup> and 0.1 M EDTA (>90% of the complex exists as the ion pair) yield 580  $\pm$  30 ns, which is also within experimental error of that of the free complex. In spite of the spectral and photophysical simi-

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larities, formation of the ion pair is crucial to prevention of the back-reaction.

In 0.1 N H<sub>2</sub>SO<sub>4</sub>, EDTA is protonated and neutral. Consequently, ion pairing is negligible and photolysis does not lead to the net formation of  $MV^+$ . The quantum yield of  $MV^+$  formation during a 450-nm photolysis of a  $0.1 \text{ N H}_2SO_4$  solution containing  $10^{-4}$  M Ru(bpy)<sub>3</sub><sup>2+</sup>,  $10^{-2}$  M MV<sup>2+</sup>, and  $10^{-2}$  M EDTA is  $\le 10^{-5}$ . In the absence of  $H_2SO_4$ , ion pairing occurs and photolysis of identical concentrations of the reagents leads to immediate formation of MV<sup>+</sup> with  $\phi = 0.09 \pm 0.02$ . Although the reduction of  $10^{-4}$  M Ru(bpy)<sub>3</sub><sup>3+</sup> by  $10^{-2}$  M EDTA occurs within the time of mixing in 0.1 N H<sub>2</sub>SO<sub>4</sub>, the pH dependence of the oxidation potential of EDTA must be considered. For this reason, additional experiments were performed in solutions buffered to pH 7 with EDTA complexed by Fe<sup>2+</sup>. The oxidation potential of FeEDTA<sup>2-</sup>, 0.117 V, is independent of pH over the 2-10 range,<sup>13</sup> and reduction of 10<sup>-4</sup> M Ru(bpy)<sub>3</sub><sup>3+</sup> by 10<sup>-3</sup> M FeEDTA<sup>2-</sup> occurs within the time of mixing. Yet, irradiation of deaerated, pH 7, aqueous solutions containing  $10^{-4}$  M Ru(bpy)<sub>3</sub><sup>2+</sup>,  $10^{-2}$  M EDTA,  $10^{-2}$  M Fe<sup>2+</sup>, and  $10^{-2}$  M MV<sup>2+</sup>, where the concentrations of free Fe<sup>2+</sup> and EDTA are calculated to be 9.6  $\times$  10<sup>-6</sup> M, does not lead to MV<sup>+</sup> formation ( $\phi \le 10^{-3}$ ), whereas in the absence of Fe<sup>2+</sup>, MV<sup>+</sup> is immediately formed.

Static scavenging of  $Ru(bpy)_3^{3+}$  by EDTA within the solvent cage implies some form of association prior to photoactivation. The data gathered here establish the formation of a 1:1 ion pair which retains the spectral and photophysical properties of the free complex. The above photochemical experiments as well as the more detailed experiments of Hoffman and Mandal<sup>4</sup> suggest that formation of the ion pair is crucial to the prevention of the back-reaction.

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Registry No. Ru(bpy)<sub>3</sub><sup>2+</sup>, 15158-62-0; EDTA<sup>2-</sup>, 32446-51-8; MV<sup>+</sup>, 1910-42-5; H<sub>2</sub>O, 7732-18-5.

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

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The stereochemistry of translationally excited bromine-for-halogen substitution was studied in gaseous 2(S)- and 2(R)halopropionyl halides. Net inversion of configuration was observed for <sup>75</sup>Br-for-X substitutions with a trend of increasing inversion as the displaced atom was varied in the series, X = F, Cl, Br. A correlation with previous studies on <sup>18</sup>F-for-X and <sup>34m</sup>Cl-for-X substitutions also showed increased inversion with increased mass of the displacing agent. In addition, these recoil atom substitutions showed an apparent independence from the free-energy requirement of reaction.

#### Introduction

One of the mechanistically important questions in recoil atom chemistry concerns retention vs. inversion of configuration in homolytic substitution  $(S_{HH}^2)$ 

$$\mathbf{X}^{*}_{i} + \mathbf{R}\mathbf{X}_{j} \xrightarrow{\mathbf{X}_{i} \text{ for } \mathbf{X}_{j}} \mathbf{R}\mathbf{X}^{*}_{i} + \mathbf{X}_{j}$$

\*Brookhaven National Laboratory. <sup>‡</sup>University of Nebraska—Lincoln. by recoil atoms at sp<sup>3</sup>-hybridized carbon in the gas phase. Resolution of this point can provide insight into the dynamics of hot-atom substitution reactions.

Presented in Tables I and II are results of previous studies of recoil tritium-for-hydrogen<sup>1-7</sup> and recoil halogen-for-halogen<sup>8-18</sup>

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TABLE I: Previous Recoil Tritium-for-Hydrogen Substitution Studies at Chiral Carbon Atoms

	substrate	% retention	
phase	molecule	of configuration	ref
gas	D-2-butanol	90	1
	L-2-butanol	95	1
	dl-2,3-dichlorobutane	93	2
	meso-2,3-dichlorobutane	80	2
	dl-1,2-dichloro-1,2-difluoroethane	97.6	3
	meso-1,2-dichloro-1,2-difluoroethane	99.5	3
	dl-1,2-dichloro-1,2-difluoroethane	96	4
	meso-1,2-dichloro-1,2-difluoroethane	96	4
liquid	dl-2,3-dichlorobutane	97.7	2
	dl-1,2-dichloro-1,2-difluoroethane	80.4	3
	meso-1,2-dichloro-1,2-difluoroethane	94	3
	dl-1,2-dichloro-1,2-difluoroethane	80	4
	meso-1,2-dichloro-1,2-difluoroethane	92	4
	glucose	99	6
	L-alanine (aqueous solution)	85	5
	dl-2,3-dichlorobutane	95.5	2
	solid glucose	99	6
	L-alanine	95	5
	dl-2,3-dichlorobutane	95.5	7

substitution at asymmetric carbon atoms in gas, liquid, and solid systems. All recoil tritium substitution reactions, regardless of substrate molecules studied or phase, occur with predominant retention of configuration. Previous gas-phase substitutions by recoil fluorine,<sup>8</sup> chlorine,<sup>4,9,10</sup> bromine,<sup>2,11</sup> and iodine<sup>11</sup> atoms on substrate molecules containing two chiral centers were also observed to yield high levels of retention. Subsequent studies, however, on the gas-phase substitution of <sup>34m</sup>Cl on substrate molecules possessing a single chiral center have yielded significantly higher levels of inversion.<sup>13,19</sup> Condensed-phase studies on the same systems yielded results that were not clear-cut. An overall decrease was observed in the level of retention for those substitutions occurring on substrates possessing two chiral centers.<sup>14-17</sup> On the other hand, condensed-phase substitutions on substrates possessing a single chiral center yielded levels of retention that were higher than the gas-phase results.<sup>12,18</sup>

Rowland et al.<sup>5,6</sup> investigated the stereochemistry of recoil tritium atom reactions in crystalline glucose and L-alanine. Because of cage effect complications in a crystal lattice, their results depicting predominant retention of configuration could not be generalized. Henchman and Wolfgang<sup>1</sup> studied the stereochemistry of recoil tritium atom substitution in chiral 2-butanol in the gas phase and reported 91% retention of configuration at the chiral center. These authors considered three possible mechanisms for the hot substitution process: (1) a direct front-side attack by the recoil tritium atom on hydrogen leading to retention of configuration, (2) back-side attack with the collision time being long enough to allow relaxation of configuration leading to inversion, and (3) formation of a metastable intermediate which could lead

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TABLE II: Previous Recoil Halogen-for-Halogen Substitution Studies at Chiral Carbon Atoms

			% retention	
	recoil	substrate	of	
phase	halogen	molecule	configuration	ref
gas	<sup>18</sup> F	dl-1,2-dichloro-	90	8
		1,2-difluoroethane		
		meso-1,2-dichloro-	90	8
		1,2-difluoroethane		
	<sup>38</sup> Cl	dl-1,2-dichloro-	91	4
		1,2-difluoroethane		
		meso-1,2-dichloro-	92	4
		1,2-difluoroethane		
	<sup>38</sup> Cl	dl-2,3-dichlorobutane	93	9,
				10
		meso-2,3-dichlorobutane	95	
	<sup>80m</sup> Br	dl-2,3-dichlorobutane	90	2
	<sup>80</sup> Br(IT)	dl-2,3-dichlorobutane	70	11
		meso-2,3-dichlorobutane	78	
	$^{125}I(EC)$	dl-2,3-dichlorobutane	64	11
	<sup>34m</sup> Cl	2(S)-chloro-4-methyl-	59	13
		valeryl chloride		
	<sup>34m</sup> Cl	2(S)-fluoropropionyl	29	19
		fluoride		
		2(S)-fluoropropionyl	27	19
		chloride		
	<sup>34m</sup> Cl	2(S)-chloropropionyl	23	19
	•.	fluoride		
	<sup>34m</sup> Cl	2(S)-chloropropionyl	19	19
	24	chloride		
	<sup>34m</sup> Cl	2(R)-chloro-1-propanol	20	13
	<sup>34m</sup> Cl	2(S)-chloro-1-propanol	21	13
liquid	"Cl	dl-2,3-dichlorobutane	75	14
	<sup>3</sup> °Cl	dl-2,3-dichlorobutane	67	15
	10	meso-2,3-dichlorobutane	60	15
	"Cl	dl-1,2-dichloro-	65	16
	80	1,2-difluoroethane		
	<sup>80</sup> Br	meso-2,3-dichlorobutane	60	17
	(or <b>B</b> t)			
	80mm	<i>dl</i> -2,3-dichlorobutane	50	17
	126T	<i>al-2,3-</i> dichlorobutane	58	14
	<sup>120</sup> I	<i>dl-2</i> ,3-dichlorobutane	54	14
	CI	2(S)-chloropropionyl	53	12
	3801	2(R)-chloropropionyl	52	12
		chloride	54	12
	<sup>38</sup> Cl	2(S)-chloro-1-propanol	53	18
solid	<sup>38</sup> Cl	dl-2,3-dichlorobutane	50	2
		meso-2.3-dichlorobutane	60	2
	<sup>38</sup> Cl	dl-2,3-dichlorobutane	71	15
		meso-2,3-dichlorobutane	71	15

to racemization. They discarded mechanisms 2 and 3 and concluded that the displacement of hydrogen by a recoil tritium atom had occurred with retention of configuration. One of the surprising aspects of this work, and that of others, is that, even though there were significant contributions of the opposite isomer, a contribution to a Walden inversion channel was dismissed for various reasons such as experimental error, low activity, radiation damage, etc.<sup>1</sup>

In stereochemical studies involving high-energy halogen-forhalogen substitution in compounds with single chiral centers, Wolf et al.<sup>12b,13,19</sup> reacted recoil <sup>34m</sup>Cl, <sup>38</sup>Cl, and <sup>18</sup>F atoms, through energetic halogen substitution at the chiral centers of 2-(S)- and 2-(R)-halopropionyl halides, 2-chloro-4-methylvaleryl chloride, and 2-chloro-1-propanol. These studies suggested that hot homolytic substitution  $(S_{HH}^2)$  reactions at sp<sup>3</sup>-hybridized carbon in the gas phase 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 to which these channels occur is dependent on the mass of the recoil atom, steric hindrance to 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>20</sup> for eneretic tritium

<sup>(6)</sup> Keller, H.; Rowland, F. S. J. Phys. Chem. 1958, 62, 1373

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<sup>(20)</sup> Tang, Y.-N.; Lee, E. K. C.; Tackikawa, E.; Rowland, F. S. Phys. Chem. 1971, 75, 1290.

atoms may have importance in the substitution process, namely, bond energy, electronegativity, and electron density. It was suggested that the most critical factor controlling the degree of inversion is the mass of the incoming atom.<sup>19</sup> This being the case, the present studies on the gas-phase substitution of recoil bromine-for-halogen at the chiral centers of 2-halopropionyl halides should occur mainly with inversion of configuration.

### Experimental Section

The experimental techniques employed have been described previously<sup>12,13</sup> by us. The 2(S)- and 2(R)-fluoropropionic acids were prepared according to the methods described by Olah et al.<sup>21,22</sup> The method described by Fu et al.<sup>23</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, benzøyl chloride, or benzoyl bromide in a distillation apparatus submerged in an oil bath previously heated to about 120 °C. The halopropionyl halide was distilled quickly to obtain a crude acid extract that was then fractionally distilled. 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 utilizing a 33-MeV <sup>3</sup>He beam to bring about the <sup>75</sup>As(<sup>3</sup>He,3n)<sup>75</sup>Br nuclear reaction ( $t_{1/2}$ for <sup>75</sup>Br is 98 min).<sup>24</sup> Radionuclidic purity was measured as being greater than 96%, using decay curve analysis and  $\gamma$ -ray spectroscopy. (The major impurities were <sup>74</sup>Br,  $t_{1/2} = 42$  min, and <sup>76</sup>Br,  $t_{1/2} = 16.2$  h.) All <sup>75</sup>Br substitution studies utilized mixtures of the appropriate 2-halopropionyl halide and arsine. Samples were prepared for irradiation by first placing 100  $\mu$ L of the 2halopropionyl halide into a preevacuated 30-mL guartz irradiation target and outgassing the sample several times. Arsine gas was then co-condensed into the same target to yield a partial pressure of 55 Torr. The targets were then heated on the cyclotron beam line to the boiling point of the particular acyl halide such that a partial pressure equivalent to 1 atm was obtained. Samples were generally irradiated with a 1  $\mu$ A <sup>3</sup>He beam to an average dose of 60  $\mu$ A s.

After irradiation, the acyl halides were allowed to react with 2(S)-valine methyl ester. The resulting diastereomers were separated by (Perkin-Elmer Sigma-1 Analyzer) GLPC using a 20 ft  $\times 1/4$  in. o.d. glass column packed with 17% carbowax 20M on Anakrom Q 80/100 mesh. The initial oven temperature was 100 °C, programmed with a 5 °C/min temperature increase to a final temperature of 175 °C. A helium flow rate of 100 mL/min for 2-fluoropropionyl fluoride and 2-chloropropionyl chloride systems was employed. The S,R and S,S diastereomers of N-(2-fluoropropionyl)-(S)-valine methyl ester eluted at 37 and 43 min, respectively, while the S, R and S, S diastereomers of N-(2chloropropionyl)-(S)-valine methyl ester eluted at 51 and 60 min, respectively. For separations in the 2-bromopropionyl bromide system, an 8 ft  $\times 1/4$  in. o.d. glass column was used that was packed with the same material. The initial oven temperature was 100 °C, programmed with a 5 °C/min temperature increase to a final temperature of 145 °C. The S,R and S,S diastereomers of N-(2-bromoproponyl)-(S)-valine methyl ester eluted at 97 and 114 min, respectively.

Absolute yields for <sup>75</sup>Br-substitution reaction products were measured for first trapping individual product peaks on charcoal as they eluted from the column. These samples were counted for <sup>75</sup>Br activity by using a well-type NaI(Tl) scintillation crystal. Decay and fraction corrections were applied to these activities, and yields were based on the total extracted <sup>75</sup>Br activity produced in the target.

TABLE III: Yields of <sup>75</sup>Br-for-F, <sup>75</sup>Br-for-Cl, and <sup>75</sup>Br-for-Br Substitution at the Chiral Carbon of (+)-2(S)- and (-)-2(R)-Halopropionyl Halides in the Gas Phase <sup>a</sup>

enantiomer	absolute yield, %	% inversion
(-)-2( <i>R</i> )-CH <sub>3</sub> CHFCOF	$4.3 \pm 0.3$	$67 \pm 2$
(+)-2( <i>S</i> )-CH <sub>3</sub> CHFCOF	$4.1 \pm 0.3$	$63 \pm 2$
(-)-2( <i>R</i> )-CH <sub>c</sub> HClCOCl	$5.5 \pm 0.3$	$75 \pm 1$
(+)-2( <i>S</i> )-CH <sub>3</sub> CHClCOCl	$5.3 \pm 0.4$	$71 \pm 2$
(−)-2( <i>R</i> )-CH <sub>3</sub> CHBrCOBr	$8.6 \pm 0.4$	$84 \pm 2$
(+)-2( <i>S</i> )-CH <sub>3</sub> CHBrCOBr	$8.8 \pm 0.6$	$81 \pm 2$

<sup>a</sup> All values were measured at 1 atm partial pressure exerted by the substrate.

TABLE IV: Yields of <sup>18</sup>F-for-Cl, <sup>34m</sup>Cl-for-Cl, and <sup>75</sup>Br-for-Cl Substitution at the Chiral Carbon of (+)-2(S)-Chloropropionyl Chloride in the Gas Phase

substitution reaction	substrate press., torr	absolute yield, %	% inversion
<sup>18</sup> F-for-Cl	500ª	1.1 ± 0.1	$35 \pm 2^{a}$
<sup>34m</sup> Cl-for-Cl	800	$2.4 \pm 0.9$	$63 \pm 7^{b}$
<sup>75</sup> Br-for-Cl	760	$5.3 \pm 0.4$	$71 \pm 2$

<sup>a</sup>Although the available <sup>18</sup>F-for-Cl data were obtained at a somewhat lower pressure for this comparison, very little pressure effect was observed in this range (see ref 19). <sup>b</sup>Reference 12.

Control experiments similar to the ones previously reported<sup>12b,13,19</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 employing <sup>75</sup>Br showed that isotopic exchange reactions at the chiral center were not significant under the conditions employed for the derivatization of the diastereomers.

### Results

The yields and percent inversion are given in Table III for <sup>75</sup>Br-for-F, <sup>75</sup>Br-for-Cl, and <sup>75</sup>Br-for-Br substitution at the asymmetric carbon of (+)-2(S)- and (-)-2(R)-halopropionyl halides in the gas phase. These results clearly coincide with trends observed in our previous studies<sup>12,13</sup> for recoil chlorine substitution at the chiral centers of 2-halopropionyl halides and 2-chloro-1propanol where predominant inversion was observed.

## Discussion

If two reaction channels are indeed operating in recoil halogen substitution reactions,<sup>19</sup> then recoil <sup>75</sup>Br reactions should proceed in a manner comparable to the parameter variations observed previously. For substrate molecules which have low steric hindrance to attack at the chiral center, factors controlling the degree of inversion of configuration include the mass of the recoil (incoming) atom and the mass of the displaced atom. A reactive collision with inversion of configuration involves back-side attack in which the relaxation time (the time necessary for energy repartition into internal degrees of freedom of the intermediate) is long enough to allow for the necessary motions of the substituents. In view of the rationale presented in previous work,<sup>19</sup> it would be expected that increasing mass of the incoming atom leads to even greater configuration interchange. The present studies on recoil <sup>75</sup>Br substitutions at the chiral centers of the 2-halopropionyl halides have clearly demonstrated this trend relative to that of  $^{18}\mathrm{F}$  or  $^{34\mathrm{m}}\mathrm{Cl}.$  Effects of the impinging recoil atom mass on the configuration subsequent to substitution are apparent in the direct comparison of data on <sup>18</sup>F-for-Cl, <sup>34m</sup>Cl-for-Cl, and <sup>75</sup>Br-for-Cl substitutions on (+)-2(S)-chloropropionyl chloride. Results in Table IV show two extremes in inversion, with a trend of increasing inversion with increasing recoil atom mass. The yields of the substitution products also increased with increasing mass of the incoming recoil atom, but this may be attributable to the increased lifetime of reaction intermediates leading to products. Care must

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<sup>(23)</sup> Fu, S.-C. J.; Birnbaum, S. M.; Greensteen, J. P. J. Am. Chem. Soc. 1954, 76, 6054.

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Figure 1. Effect of the C-X chemical bond strength on the extent of inversion from free-energy neutral X-for-X substitutions.

be taken in drawing correlations between mass and stereochemistry, as the free energies of these reactions are by no means equivalent.

The energy requirements of these substitution reactions were addressed as potential factors directing the extent of inversion. On the one hand, it was possible to probe the effect of chemical bond strength on the extent of configuration change by plotting the percent inversion as a function of the C-X bond strength of the displaced atom for substitution reactions having zero free energy ( $\Delta F = 0$ ) requirements. In Figure 1, data for the <sup>18</sup>F-for-F and <sup>34m</sup>Cl-for-Cl substitutions were taken from our previous studies.<sup>12,19</sup> Data on the T-for-H substitution on the single chiral center of 2-butanol were taken from an earlier study of Wolfgang et al.<sup>9</sup> There is a considerable discontinuity in Figure 1 that suggests the bond strength of the displaced atom is not important in controlling the configuration change. As will be seen later, the free-energy requirements of these substitution reactions also do not affect the above interchange. Intuitively, this seems reasonable since the impinging recoil atoms will carry an excess of kinetic energy into the reaction coordinate that should overwhelm any energy constraints on the reaction.

As previously pointed out, variation in the mass of the displaced atom could yield changes in the extent of inversion in part through changes in the steric hindrance to attack of the recoil atom at the sp<sup>3</sup>-hybridized carbon, and in part through changes in the lifetime of the complex intermediate formed. A reduced mass correlation allows us to perceive the kinematics of the atom-molecule encounter as involving a single mass (equivalent to the reduced mass) having relative motion about a fixed center of force.<sup>25</sup> The passage of the center of this mass through the center of force represents the coordinate for reaction, and is the same for all systems. If the time necessary for this event is also fixed (i.e. the relative velocities of the collision partners are the same irrespective of their masses), then an increase in the reduced mass value can be interpreted to mean that the atom-molecule encounter occurs sooner in this time period of reaction. In other words, the complex intermediate occupies a greater portion of the reaction coordinate and the probability for intramolecular motions yielding an inverted configuration is increased. Likewise, a smaller reduced mass means the atom-molecule encounter occurs later in the reaction period. Therefore, the intermediate is only very short-lived and does not have the opportunity to invert. Even so, the above time factor cannot be considered fixed since heavier collision partners



Figure 2. Plot of the percent inversion as a function of the reduced mass for <sup>75</sup>Br-for-X and <sup>18</sup>F-for-X substitutions:  $X = F(\blacksquare)$ , Cl( $\textcircled{\bullet}$ ), Br( $\textcircled{\bullet}$ ).



Figure 3. Correlation of the percent inversion to reduced mass for free-energy neutral X-for-X substitutions.

tend to undergo slower motions at the same energy relative to lighter components. Therefore, intermediates generated in systems with larger reduced masses not only occupy larger portions of the reaction coordinate, but also represent a greater span of time.

This parameter was tested in two cases. First, the percent inversion arising from <sup>75</sup>Br-for-X and <sup>18</sup>F-for-X (X = F, Cl, Br) substitutions on (+)-2(S)-halopropionyl halides was plotted as a function of the reduced mass in Figure 2. The extent of inversion increased linearly for both systems as the reduced mass increased. This observation lends support to the above hypothesis. In view of the energy considerations, where <sup>75</sup>Br-for-Br is free-

<sup>(25)</sup> Levine, R. D.; Bernstein, R. B. Molecular Reaction Dynamics; Oxford University Press: New York, 1974; pp 16-48.

energy neutral and <sup>75</sup>Br-for-X (X = F, Cl) are endothermic reactions, the observed linear correlation in Figure 2 also suggests that the free-energy requirements of these substitution reactions do *not* play a role in determining the extent of inversion. The same point can be made concerning the <sup>18</sup>F-for-X substitutions where the same dependence is observed between the free-energy neutral <sup>18</sup>F-for-F substitution and the exothermic <sup>18</sup>F-for-X (X = Cl, Br) substitutions.

A second correlation depicting the reduced mass effect can be seen in Figure 3 where the percent inversion was plotted as a function of the reduced mass only for those substitution reactions that are free-energy neutral. Data from the *same* four systems depicting a considerable discontinuity in the chemical bond strength plot (see Figure 1) are presented here and include T, <sup>18</sup>F, <sup>34m</sup>Cl, and <sup>75</sup>Br. A fairly good correlation was obtained, showing a trend of increased inversion with increasing reduced mass.

A feature that cannot be removed from the reduced mass correlation is the steric hindrance to the incoming atom preventing direct substitution. Unfortunately, this effect depends on the size of the displacing and displaced atoms involved and scales accordingly with the reduced mass. Therefore, one cannot rule out this effect as a significant factor in determining the configuration of the final product. A future study that will hopefully provide such a distinction will measure the extent of inversion as a function of the atomic size for systems having the *same* reduced mass. This would ensure identical collision times and afford the *same* probability for the complex intermediates to invert.

## Conclusions

Results from the present investigation lend additional support to the premise that gas-phase  $S_{HH}^2$  reactions can occur by either front-side or back-side attack. In the case where these substitutions proceed at the single chiral centers of 2(S)- and 2(R)-halopropionyl halides, the specific distribution of configurations in the substitution produces was observed to have a strong dependence on the reduced mass which is based, in part, on steric hindrance and, in part, on the lifetime of the complex intermediate. This distribution seems to be nonetheless independent of the free-energy requirements of the substitution reaction. This may be a characteristic inherent in the nuclear technique employed that generates these recoil atoms with excess kinetic energy.

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**Registry No.** <sup>75</sup>Br, 14809-47-3; (*R*)-CH<sub>3</sub>CHFCOF, 87337-50-6; (*S*)-CH<sub>3</sub>CHFCOF, 87337-49-3; (*R*)-CH<sub>3</sub>CHClCOCl, 70110-25-7; (*S*)-CH<sub>3</sub>CHClCOCl, 70110-24-6; (*R*)-CH<sub>3</sub>CHBrCOBr, 103833-24-5; (*S*)-CH<sub>3</sub>CHBrCOBr, 87337-53-9; (*S*)-CH<sub>3</sub>CHBrCO<sub>2</sub>H, 57965-29-4; (*R*)-CH<sub>3</sub>CHBrCO<sub>2</sub>H, 75244-22-3; (*S*)-CH<sub>3</sub>CHClCO<sub>2</sub>H, 29617-66-1; (*R*)-CH<sub>3</sub>CHBrCO<sub>2</sub>H, 75244-22-3; (*S*)-CH<sub>3</sub>CHBrCO<sub>2</sub>H, 32644-15-8; (*R*)-CH<sub>3</sub>CHBrCO<sub>2</sub>H, 7474-05-7; (*S*)-CH<sub>3</sub>CHBrCO<sub>2</sub>H, 32644-15-8; (*R*)-CH<sub>3</sub>CHBrCO<sub>2</sub>H, 10009-70-8; PhCOF, 455-32-3; PhCOCl, 98-88-4; PhCOBr, 618-32-6; arsine, 7784-42-1.

## **Recoil Tritium Reaction in Rare Gas–Ethane Solid Mixtures at Ultralow Temperature**

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Recoil T atom reactions have been studied in Ar (or Kr or Xe)- $C_2H_6-C_2D_6$  mixtures at 11-20 and 77 K. The relative yields of hydrogen (HT + DT) increase with a decrease of ethane concentration, while those of ethane ( $C_2H_5T + C_2D_5T$ ) decrease complementarily. The results indicate that hydrogen is formed by both hot and thermal T atoms, while ethane is formed only by the hot T atoms. The thermal T atoms abstract hydrogen from ethane by quantum mechanical tunneling even at 11-20 K as well as 77 K. The H/D abstraction isotope effect for the thermal T atom reaction with  $C_2H_6$  and  $C_2D_6$  was measured at 0.2 mol % ethane in rare gas solid. The isotope effects in Ar are 1.0 at 77 K and 3.9 at 18 K, whereas those in Xe are 4.4 at 77 K and 1.0 at 20 K. The isotope effects in Kr are 1.9 at 77 K and 1.1 at 11 K. The average energy loss of hot T atoms in rare gas solid was estimated and compared with that in the gas phase.

### Introduction

Elucidation of the behavior of T atoms in solids is very important in tritium technology relevant to nuclear fusion reactors as well as chemical kinetics in the solid phase. The reactions of tritium in the solid phase of rare gas are much simpler to study than those in reactor materials (such as metals and ceramics), and such studies may contribute to a better understanding of its behavior in the more complex system.

Though a number of studies have been reported on the behavior of recoil T atoms in the gas phase of rare gas,<sup>1</sup> the study of recoil tritium in the solid phase of rare gas has been limited only to a xenon-ethane system at 77 K.<sup>2</sup> Recently the behavior of H atoms

at ultralow temperatures (4-20 K) has been compared with those at 77 K.<sup>3-5</sup> Distinct differences were observed in the behavior of H atoms at the ultralow temperature and that at 77 K. Thus it is very interesting to compare the recoil tritium reaction at ultralow temperature with that at 77 K. In the present work we have studied the recoil tritium reaction at 11-20 K by use of a ultralow temperature irradiation facility of a nuclear reactor.

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