J. Phys. Chem. A **2007,** *111,* 9093−9101

Topological Characteristics of Electron Density Distribution in SSXY → XSSY (X or Y = F, Cl, Br, I) Isomerization Reactions

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Received: May 6, 2007; In Final Form: July 2, 2007

The reactions of SSXY to XSSY (X or Y = F, Cl, Br, I) have been studied at B3LYP/6-311++G(2df) and MP2/6-311++G(2df) levels based on B3LYP/6-311++G(2df) optimized geometries. There are two pathways (X or Y atom transferring) for each reaction of SSXY to XSSY(X or Y = F, Cl, Br, I). The "Atoms in Molecules" theory has been applied to analyze the topological characteristics of electron density distribution along the reaction path. (a) The S−S−X or S−S−Y ring structure transition region (STR) is contributed to S(1)−X or S(1)−Y bond formation and S(2)−X or S(2)−Y bond annihilation. The STR and structure transition state (STS) are defined. (b) Comparing the two pathways of each SSXY → XSSY (X, Y = F, Cl, Br, I) reaction, X or Y atom transferring, the broader the STR is, the later the STS appears, and the pathway is easier. (c) When X linked to the same S site of a three-member ring (S−S−F, S−S−Cl, S−S−Br, or S−S−I), the ring STR becomes broader and the STS appears later according to the sequence of X = F, Cl, Br, and I. And in these cases, for exothermic reactions, the higher the ΔE(P→TS1) is, the broader the STR is and the later the STS appears. (d) When the same Y atom linked to different three-member-ring S−S−X, the STR becomes broader and the STS appears later according to the sequence of X = F, Cl, Br, and I in the ring. And in these cases, for exothermic reactions, the lower the ΔE(P→TS2) is, the broader the STR is and the later the STS appears.

I. Introduction

The AIM theory,[1−7] which is rooted in quantum mechanics, generates a variety of important concepts, such as the critical points, bond path, the gradient path of electron density, and Laplacian of electron density. In the past several years, the AIM theory has been widely applied to study the electronic structures of molecules, chemical bonds, and chemical reactions.[1−13] Although in some instances[14−17] the existence of a bond critical point (BCP) is not a sufficient condition for the presence of bonding interactions, the AIM theory plays particular predominance in describing the changes of the chemical bond along the reaction path.[9−13] On the basis of catastrophe theory,[1,5] Bader et al. pointed out that for a simple ABC system a two-dimensional cross section of the structure diagram can be used to predict the existence of conflict-type and bifurcation-type mechanisms.[1−6] The reaction path from FON to FNO[9] was studied; the changes in molecular structure were presented from the viewpoint of topological analysis of electron density. The reaction of lithium amide with methane[10] was studied with ab initio calculations and the electron density analysis and the nature and evolution of the bonds were monitored throughout the reaction and related to the accompanying changes in the behavior of the charge density at the BCPs and in the properties of the individual atoms. In our previous works,[11−13] some typical reactions have been studied, emphasizing the structure changes along the reaction pathways. The T-shaped conflict structure transition state (STS) that includes a bond path linking a nuclear and a BCP as well as the kind of bifurcation type ring structure transition region (STR) enveloped by some bond paths and three or more nuclei have been discussed. We put forward the concept of STR and STS. For clarity, the traditional transitional state that is the maximum on the reaction pathway is called the "energy transition state" (ETS).

Due to their importance in atmospheric chemistry and biochemistry, the disulfides XSSX and respective isomers SSX_2 (X = H, CH_3, F, Cl, etc.) were actively studied.[18−37] Although most S_2X_2 systems exist in the disulfide form (XSSX, C_2 symmetry), isomeric thiosulfoxide structures (SSX_2, C_s symmetry) are also found. The two isomers of disulfur difluoride (i.e., FSSF and SSF_2) have been isolated, identified, and confirmed.[35−37] When the S_2F_2 and ClSSCl were mixed, the compound SSFCl was produced. Until now, there are few studies on the SSXY and isomers XSSY (X or Y = F, Cl, Br, I).[38,39]

In this paper, the reactions of SSXY to XSSY (X or Y = F, Cl, Br, I) have been studied. The aim of this paper is to extend our previous works[11−13] to SSXY and XSSY model isomerization reactions, focusing on the changing trends of the bifurcation-type ring STR and the corresponding STS in the framework of the AIM theory, to understand more about the relationship between topological characteristics of electron density distribution and the energy variation along the reaction, to explore the changing trends of the width of the STR and the position of the STS with different atoms linked to the same three-membered ring or different three-membered rings linking with the same atom.

II. Methods of Calculation

The DFT (B3LYP)[40,41] calculations have been carried out with the Gaussian 98 package of programs,[42] using the 6-311++G-(2df) basis set. For the element iodine, the quasirelativistic effective core potentials (ECPs) basis set[43] was used, which

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10.1021/jp073455k CCC: $37.00

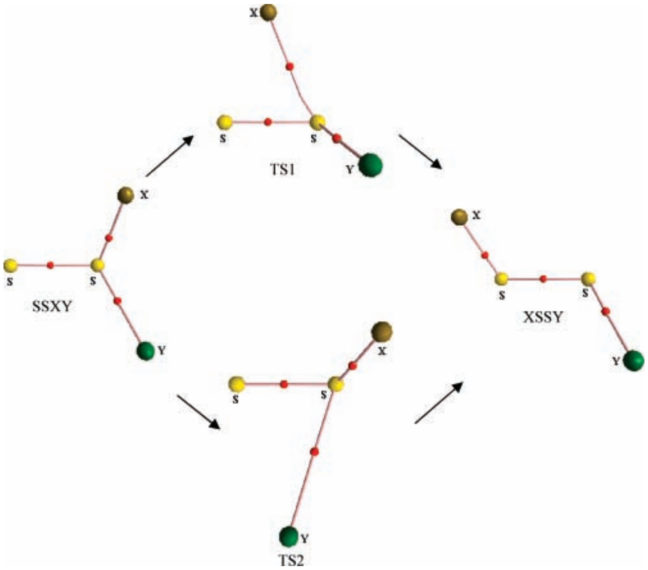


Figure 1. Structure changes of SSXY → XSSY (X, Y = F, Cl, Br, I) reactions.

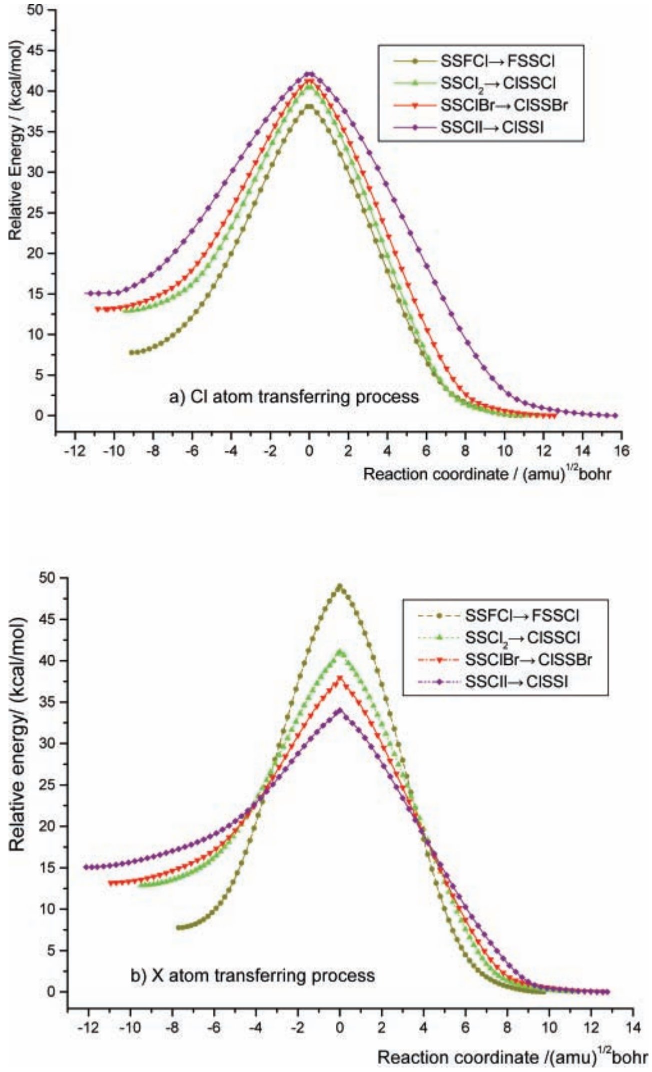


Figure 2. Potential energy curves of SSClX → XSSCl (X = F, Cl, Br, I) reactions. [The energies of product XSSCl (X= F, Cl, Br, I) are given as zero.]

includes two of the most important relativistic effects, the mass velocity and Darwin contributions, and it has been used successfully in calculating ionization energies and reaction energies.[12,43,44] The d polar functions were split into $\alpha_1(d_{polar}) = 0.604$ and $\alpha_2(d_{polar}) = 0.151$ in this work.

The geometries of the reactants, transition states, and products presented were fully optimized at the level of theory mentioned above, with constrained C_s symmetry for SSX_2 (X = F, Cl, Br, I) and C_2 for XSSX (X = F, Cl, Br, I). Vibrational analyses were used to check the nature of the stationary points. The reaction path has been followed by using Fukui's theory of the intrinsic reaction coordinate (IRC) method[45] in mass-weighted internal coordinates going in the forward and reverse directions from the transition state with the step size of 0.01 (amu)$^{1/2}$ bohr. Energies of the stationary points are calculated at the B3LYP/6-311++G(2df) and MP2/6-311++G(2df) levels based on the B3LYP/6-311++G(2df) optimized geometries. The topological analyses have been performed on B3LYP/6-311++G(2df) densities, using the AIM 2000 program.[46] The molecular graphs (Figure 1 and 3) along the IRC pathways were plotted by using the AIM 2000 program.[46]

III. Results and Discussion

A. Geometrical Description and Potential Energy Curves. Calculations on geometries of the reactants SSXY, products XSSY (X, Y = F, Cl, Br, I), and transition states TS1 and TS2 (see Figure 1) have been performed at the theoretical levels described in the methodology. The optimized geometries of SSX_2 (X = F, Cl, Br, I) belong to C_s symmetry and XSSX (X = F, Cl, Br, I) belong to C_2 symmetry. The geometries of the other reactants, products, and all of the transition sates belong to C_1 symmetry. IRC calculations were carried out to validate the connections of reactants SSXY, transition states, and products XSSY (X, Y = F, Cl, Br, I). Along all the reaction paths, there is no breakage of the S−S bond. When X and Y are different atoms, there are two transition states (TS1and TS2) for each SSXY → XSSY (X, Y = F, Cl, Br, I) reaction, one is on the X transferring pathway, and the other is on the Y transferring pathway.

The geometric parameters are presented in Table 1a−d for SSXY → XSSY reactions (X, Y = F, Cl, Br, I), respectively. For comparison, in the SSFX → XSSF (X = F, Cl, Br, I) reaction, the transition states via F atom transferring are named TS1 and those via X transferring are named TS2; in the SSClX → XSSCl (X = F, Cl, Br, I) reaction, the transition states via Cl atom transferring are named TS1 and those via X transferring are named TS2; in the SSXBr → XSSBr (X = F, Cl, Br, I) reaction, the transition states via Br atom transferring are named TS1 and those via X transferring are named TS2; in the SSXI → XSSI (X = F, Cl, Br, I) reaction, the transition states via I atom transferring are named TS1 and those via X transferring are named TS2, respectively.

For the SSFX → XSSF reaction (see Table 1a), the S−S bond length in reactants SSFX (X = F, Cl, Br, I), TS1, TS2, and products XSSF (X = F, Cl, Br, I) becomes longer according to the sequence X = F, Cl, Br, and I. The same trends exist in the SSClX → XSSCl, SSXBr → XSSBr, and SSXI → XSSI reactions (see Table 1).

The energy of reactants, TS1, TS2, and products was summarized in Table 2. For SSF_2 → FSSF isomerization, B3LYP/6-311++G(2df)//B3LYP/6-311++G(2df) and MP2/6-311++G(2df)//B3LYP/6-311++G(2df) calculated energy differences of SSF_2 to FSSF are −1.42 and 5.07 kcal/mol. Reference 31 gives a QCISD/6-31+G**//MP2/6-31G*+ZPE energy difference of −4.8 kcal/mol, and it is found that SSF_2 and FSSF isomers have similar energies and FSSF is more stable

TABLE 1: Geometry Parameters of the Stationary Points of the Reactions (a) SSFX → XSSF (X = F, Cl, Br, I), (b) SSClX → XSSCl (X = F, Cl, Br, I), (c) SSXBr → XSSBr (X = F, Cl, Br, I), and (d) SSXI → XSSI (X = F, Cl, Br, I)[a]

(a) SSFX → XSSF (X = F, Cl, Br, I)

reactant	S−S	S(2)−F	S(2)−X	FS(2)S(1)	XS(2)S(1)	XSSF	ref
SSF_2	1.8744	1.6391	1.6391	108.0	108.0	98.0	
	(1.877)	(1.656)	(1.656)	(107.5)	(107.5)	(98.5)	47
SSFCl	1.8812	1.6507	2.1508	107.6	110.5	101.5	
		(1.640)	(2.030)				48
SSFBr	1.8826	1.6529	2.3437	107.6	111.2	102.3	
SSFI	1.8867	1.6616	2.5438	107.9	112.0	101.9	

TS1 (S−S−F ring)	S−S	S(2)−F	S(2)−X	FS(2)S(1)	XS(2)S(1)	XSSF
SSF_2 → FSSF	1.8414	2.2729	1.6227	67.0	110.0	88.9
SSFCl → FSSCl	1.8566	2.2673	2.0802	67.6	112.2	92.4
SSFBr → FSSBr	1.8586	2.2696	2.2568	67.6	112.9	93.0
SSFI → FSSI	1.8705	2.2636	2.4192	67.9	112.3	87.6

TS2 (S−S−X ring)	S−S	S(2)−F	S(2)−X	FS(2)S(1)	XS(2)S(1)	XSSF
SSF_2 → FSSF	1.8414	1.6227	2.2729	110.0	67.0	88.9
SSFCl → FSSCl	1.8533	1.6267	2.8101	109.7	72.4	92.9
SSFBr → FSSBr	1.8594	1.6306	2.9774	109.5	73.7	94.1
SSFI → FSSI	1.8677	1.6326	3.2503	109.3	75.8	97.2

product	S−S	S(1)−F	S(2)−X	FS(1)S(2)	XS(2)S(1)	XSSF	ref
FSSF	1.9110	1.6621	1.6621	108.2	108.2	88.0	
	(1.877)	(1.656)	(1.656)	(107.5)	(107.5)	(98.5)	47
FSSCl	1.9331	1.6570	2.1190	107.3	110.0	87.7	
FSSBr	1.9346	1.6559	2.2921	107.2	110.6	87.8	
FSSI	1.9540	1.6523	2.4575	106.5	110.3	87.6	

(b) SSClX → XSSCl (X = F, Cl, Br, I)

reactant	S−S	S(2)−Cl	S(2)−X	ClS(2)S(1)	XS(2)S(1)	XSSCl
SSFCl	1.8812	2.1508	1.6507	110.5	107.6	101.5
$SSCl_2$	1.8901	2.1599	2.1599	109.9	109.9	106.1
SSClBr	1.8924	2.1582	2.3542	109.8	110.6	107.2
SSClI	1.8970	2.1625	2.5627	109.9	111.3	107.0

TS1 (S−S−Cl ring)	S-S	S(2)−Cl	S(2)−X	ClS(2)S(1)	XS(2)S(1)	XSSCl
SSFCl → FSSCl	1.8533	2.8101	1.6267	72.4	109.7	92.9
$SSCl_2$ → ClSSCl	1.8698	2.8125	2.0830	73.2	111.9	96.7
SSClBr → ClSSBr	1.8718	2.8184	2.2583	73.2	112.6	97.6
SSClI → ClSSI	1.8831	2.8118	2.4294	73.5	112.8	98.3

TS2 (S−S−X ring)	S-S	S(2)-Cl	S(2)-X	ClS(2)S(1)	XS(2)S(1)	XSSCl
SSFCl → FSSCl	1.8566	2.0802	2.2673	112.2	67.6	92.4
$SSCl_2$ → ClSSCl	1.8698	2.0830	2.8125	111.9	73.2	96.7
SSClBr → ClSSBr	1.8756	2.0874	2.9797	111.8	74.5	98.0
SSClI → ClSSI	1.8842	2.0876	3.2401	111.6	76.5	99.6

product	S−S	S(1)−Cl	S(2)−X	ClS(1)S(2)	XS(2)S(1)	XSSCl	ref
FSSCl	1.9331	2.1190	1.6570	110.0	107.3	87.7	
ClSSCl	1.9577	2.1037	2.1037	109.2	109.2	87.1	
	(1.931)	(2.057)	(2.057)	(108.2)	(108.2)	(84.1)	47
ClSSBr	1.9592	2.1021	2.2756	109.1	109.7	87.0	
ClSSI	1.9802	2.0939	2.4365	108.3	109.4	87.1	

(c) SSXBr → XSSBr (X = F, Cl, Br, I)

reactant	S−S	S(2)−Br	S(2)−X	BrS(2)S(1)	XS(2)S(1)	XSSBr
SSFBr	1.8826	2.3437	1.6529	111.2	107.6	102.3
SSClBr	1.8924	2.3542	2.1582	110.6	109.8	107.2
$SSBr_2$	1.8945	2.3510	2.3510	110.6	110.6	108.4
SSBrI	1.9010	2.3552	2.5507	110.9	111.3	107.8

TS1(S−S−Br ring)	S−S	S(2)−Br	S(2)−X	BrS(2)S(1)	XS(2)S(1)	XSSBr
SSFBr → FSSBr	1.8594	2.9774	1.6306	73.7	109.5	94.1
SSClBr → ClSSBr	1.8756	2.9797	2.0874	74.5	111.8	98.0
$SSBr_2$ → BrSSBr	1.8777	2.9853	2.2631	74.5	112.5	99.0
SSBrI → BrSSI	1.8894	2.9775	2.4321	74.9	112.5	98.8

TS2 (S−S−X ring)	S−S	S(2)−Br	S(2)−X	BrS(2)S(1)	XS(2)S(1)	XSSBr
SSFBr → FSSBr	1.8586	2.2568	2.2696	112.9	67.6	93.0
SSClBr → ClSSBr	1.8718	2.2583	2.8184	112.6	73.2	97.6
$SSBr_2$ → BrSSBr	1.8777	2.2631	2.9853	112.5	74.5	99.0
SSBrI → BrSSI	1.8864	2.2632	3.2440	112.3	76.6	99.8

TABLE 1 (Continued)

product	S−S	S(1)−Br	S(2)−X	BrS(1)S(2)	XS(2)S(1)	XSSBr	ref
FSSBr	1.9346	2.2921	1.6559	110.6	107.2	87.8	
ClSSBr	1.9592	2.2755	2.1021	109.7	109.1	87.0	
BrSSBr	1.9614	2.2736	2.2736	109.7	109.7	87.1	
	(1.980)	(2.240)	(2.240)	(105.0)	(105.0)	(83.5)	49
BrSSI	1.9819	2.2629	2.4323	108.8	109.3	86.2	

(d) SSXI → XSSI (X = F, Cl, Br, I)

reactant	S−S	S(2)−I	S(2)−X	IS(2)S(1)	XS(2)S(1)	XSSI
SSFI	1.8867	2.5438	1.6616	112.0	107.9	101.9
SSClI	1.8970	2.5627	2.1625	111.3	109.9	107.0
SSBrI	1.9010	2.5507	2.3552	111.2	110.9	107.8
SSI_2	1.9076	2.5508	2.5508	111.9	111.9	107.5

TS1 (S−S−I ring)	S−S	S(2)−I	S(2)−X	IS(2)S(1)	XS(1)S(2)	XSSI
SSFI → FSSI	1.8677	3.2503	1.6326	75.8	109.3	97.2
SSClI → ClSSI	1.8842	3.2401	2.0876	76.5	111.6	99.6
SSBrI → BrSSI	1.8864	3.2440	2.2632	76.6	112.3	99.8
SSI_2 → ISSI	1.8986	3.2256	2.4276	77.0	112.3	97.5

TS2 (S−S−X ring)	S−S	S(2)−I	S(2)−X	IS(2)S(1)	XS(2)S(1)	XSSI
SSFI → FSSI	1.8705	2.4192	2.2636	112.3	67.9	87.6
SSClI → ClSSI	1.8831	2.4294	2.8118	112.8	73.5	98.3
SSBrI → BrSSI	1.8894	2.4321	2.9775	112.5	74.9	98.8
SSI_2 → ISSI	1.8986	2.4276	3.2256	112.3	77.0	97.5

product	S−S	S(1)−I	S(2)−X	IS(1)S(2)	XS(2)S(1)	XSSI
FSSI	1.9540	2.4575	1.6523	110.3	106.5	87.6
ClSSI	1.9802	2.4365	2.0939	109.4	108.3	87.1
BrSSI	1.9819	2.4323	2.2629	109.3	108.8	86.2
ISSI	2.0041	2.4169	2.4169	108.4	108.4	85.3

[a] Bond lengths in Å and bond angles in deg.

TABLE 2: Energies of the Stationary Points (in kcal/mol) at the B3LYP/6-311++G(2df) and MP2/6-311++G(2df) Levels Based on B3LYP/6-311++G(2df) Optimized Geometries

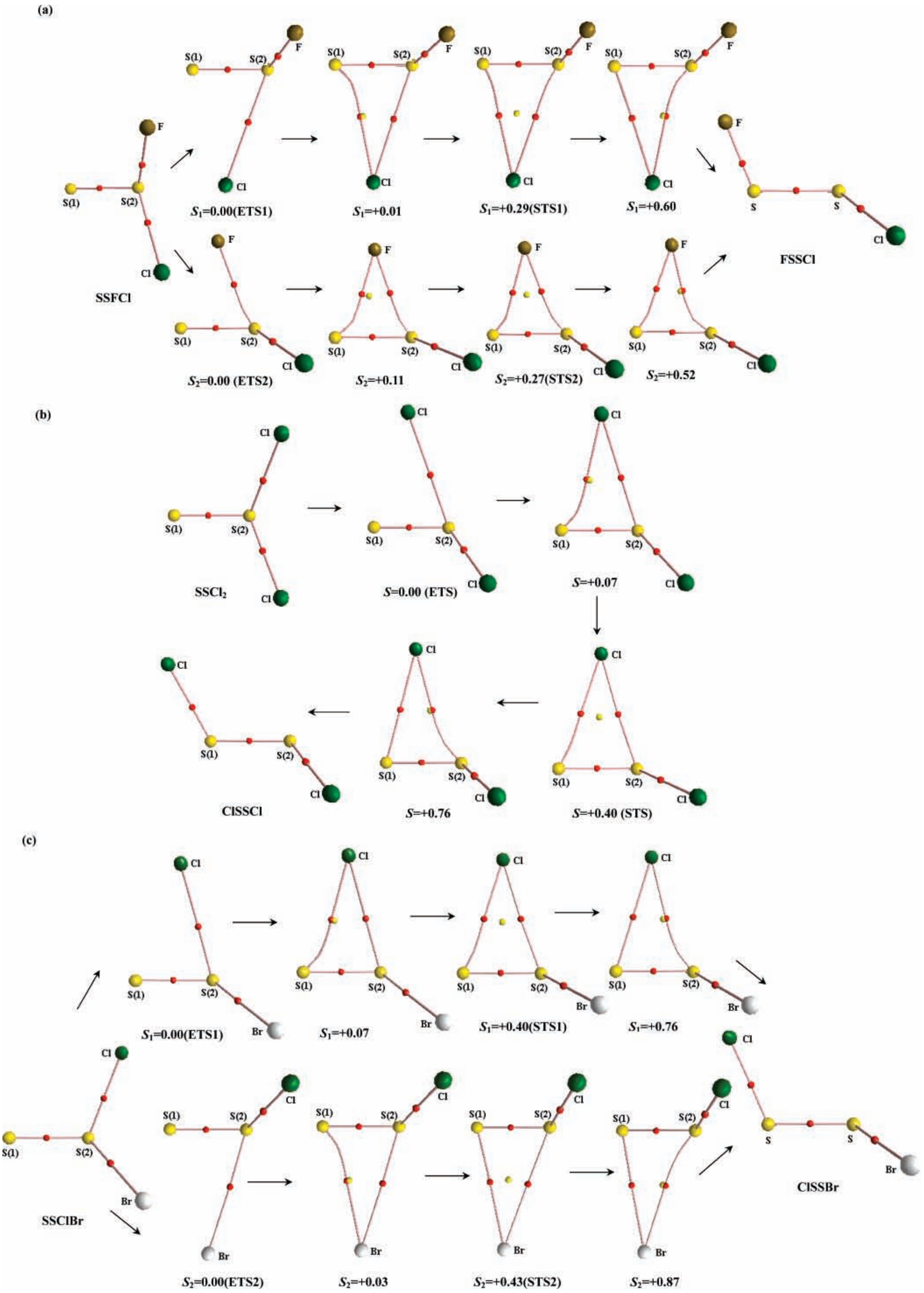
			S−S−F ring				S−S−X ring			
	Δ*E*(R→P)		Δ*E*(R→TS1)		Δ*E*(P→TS1)		Δ*E*(R→TS2)		Δ*E*(P→TS2)	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
SSF_2 → FSSF	−1.42	5.07	45.74	50.01	47.16	44.94	45.74	50.01	47.16	44.94
	(−4.8)[a]		(43.0)[a]							
SSFCl → FSSCl	−7.76	−3.32	41.61	44.32	49.37	47.64	30.97	35.93	38.73	39.25
SSFBr → FSSBr	-8.40	-4.65	41.12	43.51	49.52	48.16	27.23	30.62	35.63	35.27
SSFI → FSSI	-10.56	-8.12	39.80	41.20	50.35	49.32	21.05	23.81	31.61	31.93

			S−S−Cl ring				S−S−X ring			
	Δ*E*(R→P)		Δ*E*(R→TS1)		Δ*E*(P→TS1)		Δ*E*(R→TS2)		Δ*E*(P→TS2)	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
SSFCl → FSSCl	-7.76	-3.32	30.97	35.93	38.73	39.25	41.61	44.32	49.37	47.64
$SSCl_2$ → ClSSCl	-12.88	-11.40	28.20	32.47	41.08	41.63	28.20	32.47	41.08	41.63
SSClBr → ClSSBr	-13.17	-10.89	28.07	32.30	41.24	43.19	24.77	27.51	37.94	38.40
SSClI → ClSSI	-15.06	-14.07	27.29	30.90	42.36	44.97	18.93	20.97	34.00	35.04

			S−S−Br ring				S−S−X ring			
	Δ*E*(R→P)		Δ*E*(R→TS1)		Δ*E*(P→TS1)		Δ*E*(R→TS2)		Δ*E*(P→TS2)	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
SSFBr → FSSBr	-8.40	-4.65	27.23	30.62	35.63	35.27	41.12	43.51	49.52	48.16
SSClBr → ClSSBr	-13.17	-10.89	24.77	27.51	37.94	38.40	28.07	32.30	41.24	43.19
$SSBr_2$ → BrSSBr	-13.37	-11.40	24.71	27.51	38.08	38.92	24.71	27.51	38.08	38.92
SSBrI → BrSSI	-15.07	-14.22	24.12	26.31	39.19	40.52	19.13	21.39	34.20	35.60

			S−S−I ring				S−S−X ring			
	Δ*E*(R→P)		Δ*E*(R→TS1)		Δ*E*(P→TS1)		Δ*E*(R→TS2)		Δ*E*(P→TS2)	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
SSFI → FSSI	-10.56	-8.12	21.05	23.81	31.61	31.93	39.80	41.20	50.35	49.32
SSClI → ClSSI	-15.06	-14.07	18.93	20.97	34.00	35.04	27.29	30.90	42.36	44.97
SSBrI → BrSSI	-15.07	-14.22	19.13	21.39	34.20	35.60	24.12	26.31	39.19	40.52
SSI_2 → ISSI	-16.13	-16.22	19.26	21.06	35.39	37.28	19.26	21.06	35.39	37.28

[a] Values from ref 31 calculated at the QCISD/6-31+G**//MP2/6-31G*+ZPE level.


(a)
SSFCl
S(1)
S(2)
F
Cl
S1=0.00(ETS1)
S1=+0.01
S1=+0.29(STS1)
S1=+0.60
S2=0.00 (ETS2)
S2=+0.11
S2=+0.27(STS2)
S2=+0.52
FSSCl
S
(b)
SSCl2
S=0.00 (ETS)
S=+0.07
S=+0.40 (STS)
S=+0.76
ClSSCl
(c)
SSClBr
Br
S1=0.00(ETS1)
S1=+0.07
S1=+0.40(STS1)
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S2=+0.87
ClSSBr

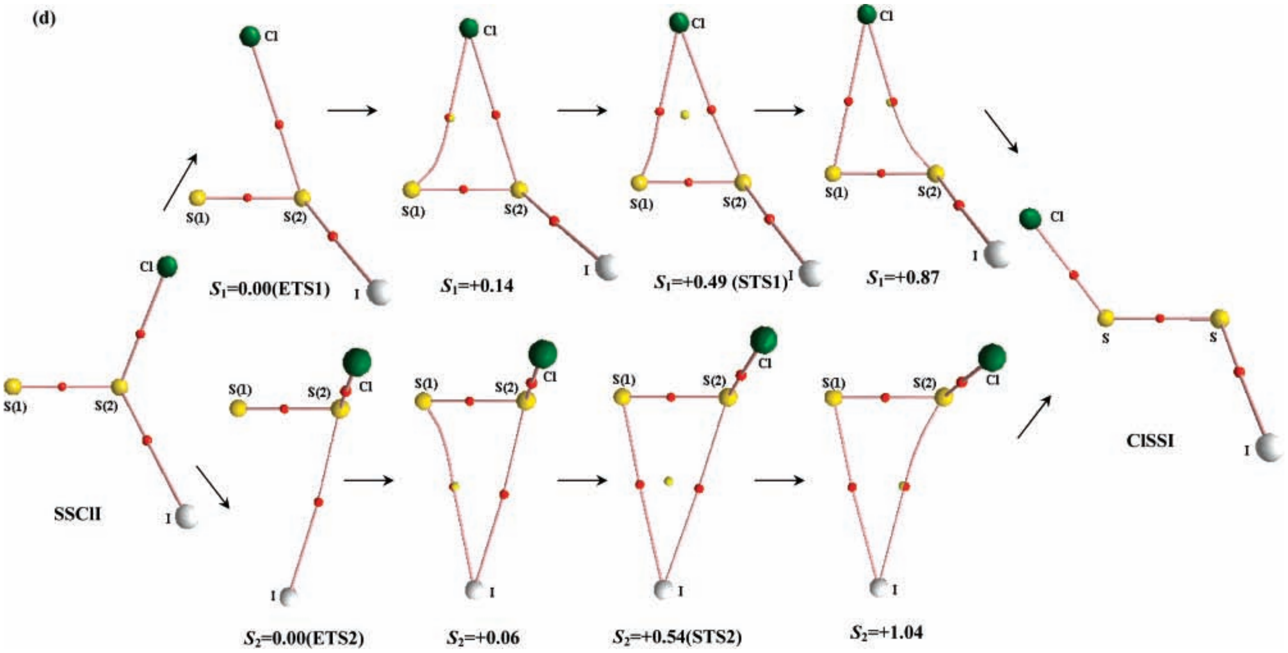

Figure 3. (a) Molecular graphs of SSFCl → FSSCl reaction. (b) Molecular graphs of $SSCl_2$ → ClSSCl reaction. (c) Molecular graphs of SSClBr → ClSSBr reaction. (d) Molecular graphs of SSClI → ClSSI reaction. For small dots, bond critical points (BCPs) are red and ring critical points (RCPs) are yellow.

at low temperature. Then, the B3LYP/6-311++G(2df)//B3LYP/6-311++G(2df) calculated energy is better than the MP2/6-311++G(2df)//B3LYP/6-311++G(2df) calculated energy in this case.

For SSF_2 → FSSF isomerization, B3LYP/6-311++G(2df)//B3LYP/6-311++G(2df) and MP2/6-311++G(2df)//B3LYP/6-311++G(2df) calculated energy barriers are 45.74 and 50.01 kcal/mol. Reference 31 gives a QCISD/6-31+G**//MP2/6-31G*+ZPE energy barrier of 43.0 kcal/mol, while experimentally (refs 22 and 35) FSSF isomerizes to SSF_2 with heating at $T > -80$ °C, thus indicating that both isomers are connected by a low-energy transition state, which is in disagreement with our calculated 45.74 kcal/mol and the QCISD/6-31+G**//MP2/6-31G*+ZPE calculated 43.0 kcal/mol from ref 31. This suggested that the isomerization might proceed via a bimolecular mechanism in which lower transition states, as explained in reference 31, are conceivable.

For the reactions of SSFCl → FSSCl, SSFBr → FSSBr, and SSFI → FSSI, the energy barrier of F atom transferring is higher than that of Cl, Br, and I atom transferring, respectively; for the reactions of SSClBr → ClSSBr and SSClI → ClSSI, the energy barrier of Cl atom transferring is higher than that of Br and I atom transferring, respectively; for the SSBrI → BrSSI reaction, the energy barrier of Br atom transferring is higher than that of I atom transferring. Then it can be concluded that for the X transferring pathway and Y transferring pathway of SSXY → XSSY (X, Y = F, Cl, Br, I) isomerization reactions, the energy barrier of the heavier atom transferring is lower than that of light atom transferring. That is, heavier atom transferring is easier than light atom transferring in the isomerization reactions SSXY → XSSY (X, Y = F, Cl, Br, I).

From Table 2, for the SSClX → XSSCl (X = F, Cl, Br, I) reactions, generally, both the Cl transferring pathway and the X transferring pathway are exothermic, and the increasing sequence amount of releasing heat is as X = F, Cl, Br, and I; the activation energy decreases as X = F, Cl, Br, and I. The potential energy curves of SSClX → XSSCl (X = F, Cl, Br, I) reactions are displayed in Figure 2, in which the energies of the products XSSCl (X = F, Cl, Br, I) are given as zero. From Figure 2 and Table 2, the energy difference from the transition state to the product in these reactions also shows a trend: for the Cl atom transferring pathway (Figure 2a), the increasing sequence of ΔE(P→TS1) in reaction path (a) is as X = F, Cl, Br, and I, while for the X transferring pathway, ΔE(P→TS2) in reaction path (b) decreases in the sequence X = F, Cl, Br, and I.

The above changing trends are applicable in the other processes of SSFX → XSSF, SSXBr → XSSBr, and SSXI → XSSI (X = F, Cl, Br, I) shown in Table 2.

B. Structure Changes on Reaction Pathways. Figure 3 shows the changes of the structure and topological properties of SSClX → XSSCl (X = F, Cl, Br, I) reactions. For the Cl atom transferring process (SSClX → TS1 → XSSCl), there exists the S−S−Cl three-membered-ring structure. For the X atom transferring process (SSClX → TS2 → XSSCl), there exists the S−S−X three-membered-ring structure. For each of the titled processes, accompanied by the X or Y atom transferring, there exists a S−S−X or S−S−Y three-membered-ring structure. (See Figure 4 and Tables 5 and 6 in the Supporting Information.)

To distinguish the reaction coordinate in different pathways, in the SSFX → XSSF (X = F, Cl, Br, I) reaction, the reaction coordinate via F atom transferring is named S_1 and that via X transferring is named S_2. Similarly, in the SSClX → XSSCl (X = F, Cl, Br, I) reaction, the reaction coordinate via Cl atom transferring is named S_1 and that via X transferring is named S_2; in the SSXBr → XSSBr (X = F, Cl, Br, I) reaction, the reaction coordinate via Br atom transferring is named S_1 and that via X transferring is named S_2; in the SSXI → XSSI (X = F, Cl, Br, I) reaction, the reaction coordinate via I atom transferring is named S_1 and that via X transferring is named S_2, respectively.

For the Cl atom transferring in the SSFCl → TS1→ FSSCl process, from SSFCl to the ETS1 ($S_1 = 0.00$), the S(2)−Cl bond becomes more and more weak and the bond path becomes more and more bent. At $S_1 = +0.01$, the S(1)−Cl bond forms and a S−S−Cl three-membered-ring structure appears. After that point the electron density $\rho(r_c)$ at the BCP of the S(2)−Cl bond becomes smaller and $\rho(r_c)$ at the BCP of the S(1)−Cl bond becomes larger, which indicates that the S(2)−Cl bond becomes weaker and the S(1)−Cl bond becomes stronger. At the point $S_1 = +0.60$, the S(2)−Cl bond will be broken and the S−S−Cl three-membered-ring structure will disappear. After that point the S(1)−Cl bond becomes stronger and stronger, and at last FSSCl forms. For the F atom transferring in the SSFCl → TS2 → FSSCl process, at the point $S_2 = +0.11$, the S(1)−F bond forms and a S−S−F three-membered-ring structure appears. At the point $S_2 = +0.52$, the S(2)−F bond will be broken and the S−S−F three-membered-ring structure will disappear. After that point the S(1)−F bond becomes stronger and stronger, and at last FSSCl forms.

For the Cl atom transferring of the $SSCl_2$ → TS → ClSSCl process, the S−S−Cl three-membered-ring structure exists in the region of $S = +0.07 \rightarrow +0.76$. For the Cl atom transferring in the SSClBr → TS1 → ClSSBr process, the S−S−Cl three-membered-ring structure exists in the region of $S_1 = +0.07 \rightarrow +0.76$. For the Br atom transferring of the SSClBr → TS2 → ClSSBr process, the S−S−Br three-membered-ring structure exists in the region of $S_2 = +0.03 \rightarrow +0.87$. For the Cl atom transferring in the SSClI → TS1 → ClSSI process, the S−S−Cl three-membered-ring structure exists in the region of $S_1 = +0.14 \rightarrow +0.87$. For the I atom transferring of the SSClI → TS2 → ClSSI process, the S−S−I three-membered-ring structure exists in the region of $S_2 = +0.06 \rightarrow +1.04$.

The structure changes of the reactions SSFX → XSSF, SSXBr → XSSBr, and SSXI → XSSI are similar with those of the SSClX → XSSCl (X = F, Cl, Br, I) process. (See Figure 4 in the Supporting Information.)

C. Definition of STR and STS. For each of the titled reactions, with the transferring of X or Y atom, there exists a S−S−X or S−S−Y three-membered-ring bifurcation-type structure. In our previous works,[12,13] we put forward the concept of STR and STS. In the ring STR, the structure where the RCP has the maximum eigenvalue λ_2 of the Hessian matrix of electron density was defined as the STS. For the bifurcation-type ring-shaped structure, we can give the definition of the STR as the region from the formation to the annihilation of the ring structure, with the eigenvalue λ_2 of RCP from zero (or close to zero) to maximum and to zero (or close to zero); the STS in STR is defined as the structure where the eigenvalue λ_2 at the RCP reaches the maximum (the u_2 vector which has the eigenvalue λ_2 is in the ring plane and tangential to the moving orientation of the RCP).

Take the Cl atom transferring of the SSFCl → TS1 → FSSCl process as an example, at the point of $S_1 = +0.01$, where the S(1)−Cl bond is formed and the RCP just appears, the λ_2 at RCP of the S−S−Cl ring structure is 0.0015 (close to zero). In the STR of $S_1 = +0.01 \rightarrow +0.29$, λ_2 of S−S−Cl RCP increases continuously. At the point $S_1 = +0.29$, λ_2 at RCP of the S−S−Cl reaches the maximum value 0.0063. After this point, the λ_2 at RCP begins to decrease. At the point $S_1 = +0.60$, where the S(2)−Cl bond will be broken and RCP will disappear, λ_2 at RCP of the S−S−Cl is 0.0013 (close to zero). The region of $S_1 = +0.01 \rightarrow +0.60$ is the region from the formation to the annihilation of the ring structure, with eigenvalue λ_2 of RCP from 0.0015 (close to zero) to 0.0063 (maximum) and to 0.0013 (close to zero). λ_2 at the S−S−Cl RCP of the point $S_1 = +0.29$ has the maximum value 0.0063. Therefore, the region of $S_1 = +0.01 \rightarrow +0.60$ is the STR and the point $S_1 = +0.29$ is the STS of the Cl atom transferring for the SSFCl → FSSCl process.

TABLE 3: Topological Properties Associated with BCPs and RCPs of the SSFCl → FSSCl Reaction Pathway

	S[a,b]	ρ[c]	λ_1[d]	λ_2[d]	λ_3[d]	$\nabla^2\rho$[e]
S−S−Cl three-membered-ring structure						
S(1)−Cl bond	+0.01	**0.0291**[f]	−0.0221	−**0.0010**[f]	0.1169	0.0938
	+0.10	0.0294	−0.0225	−0.0054	0.1169	0.0890
	+0.29	0.0303	−0.0234	−0.0098	0.1171	0.0839
	+0.40	0.0308	−0.0240	−0.0118	0.1174	0.0816
	+0.60	0.0320	−0.0251	−0.0149	0.1181	0.0781
S−S−Cl ring	+0.01	**0.0291**[f]	−0.0222	**0.0015**[f]	0.1170	0.0963
	+0.10	0.0293	−0.0226	0.0048	0.1172	0.0994
	+0.20	0.0294	−0.0230	0.0060	0.1176	0.1006
	+0.28	0.0295	−0.0233	0.0063	0.1180	0.1010
(STS1)	+0.29	0.0295	−0.0233	**0.0063**[g]	0.1181	0.1011
	+0.30	0.0295	−0.0233	0.0063	0.1182	0.1012
	+0.40	0.0294	−0.0236	0.0059	0.1190	0.1013
	+0.60	**0.0292**[h]	−0.0242	**0.0013**[h]	0.1226	0.0997
S(2)−Cl bond	+0.01	0.0321	−0.0284	−0.0150	0.1297	0.0863
	+0.10	0.0316	−0.0277	−0.0136	0.1290	0.0877
	+0.29	0.0306	−0.0265	−0.0105	0.1275	0.0905
	+0.40	0.0300	−0.0259	−0.0083	0.1266	0.0924
	+0.60	**0.0292**[h]	−0.0245	−**0.0014**[h]	0.1239	0.0980
S−S−X (X = F) three-membered-ring structure						
S(1)−F bond	+0.11	**0.0488**[f]	−0.0463	−**0.0080**[f]	0.2467	0.1924
	+0.20	0.0494	−0.0472	−0.0133	0.2489	0.1884
	+0.27	0.0499	−0.0479	−0.0164	0.2503	0.1860
	+0.40	0.0509	−0.0494	−0.0214	0.2530	0.1822
	+0.52	0.0519	−0.0509	−0.0254	0.2557	0.1794
S−S−F ring	+0.11	**0.0488**[f]	−0.0464	**0.0077**[f]	0.2419	0.2032
	+0.20	0.0490	−0.0470	0.0102	0.2421	0.2053
	+0.26	0.0491	−0.0475	0.0107	0.2430	0.2062
(STS2)	+0.27	0.0491	−0.0475	**0.0107**[g]	0.2432	0.2064
	+0.28	0.0491	−0.0476	0.0107	0.2434	0.2065
	+0.30	0.0492	−0.0477	0.0106	0.2439	0.2068
	+0.40	0.0492	−0.0484	0.0092	0.2473	0.2081
	+0.52	**0.0490**[h]	−0.0497	**0.0019**[h]	0.2570	0.2092
S(2)−F bond	+0.11	0.0518	−0.0562	−0.0245	0.2821	0.2014
	+0.20	0.0511	−0.0550	−0.0214	0.2791	0.2027
	+0.27	0.0505	−0.0541	−0.0187	0.2766	0.2038
	+0.40	0.0497	−0.0524	−0.0129	0.2713	0.2060
	+0.52	**0.0490**[h]	−0.0504	−**0.0029**[h]	0.2620	0.2087

[a] S: reaction coordinate in units of $(\mathrm{amu})^{1/2}$ bohr. [b] (+) forward direction of the reaction pathway. [c] ρ: the electron density. [d] λ_i: eigenvalues of the Hessian Matrix. [e] $\nabla^2\rho$: Laplacian of electron density. [f] The formation of the ring structure with a singularity in the density. [g] The maximum λ_2 eigenvalue of the Hessian matrix. [h] The annihilation of the ring structure with a singularity in the density

In the F atom transferring of the SSFCl → TS2 → FSSCl process, at the point of $S_2 = +0.11$, the eigenvalue λ_2 of the newly formed S−S−F RCP is close to zero ($\lambda_2 = 0.0077$). In the region of $S_2 = +0.11 \rightarrow +0.27$, λ_2 of S−S−F RCP increases continuously. At the point $S_2 = +0.27$, λ_2 of the RCP reaches the maximum. After this point, λ_2 of the RCP begins to decrease. As the reaction gets to the point $S_2 = +0.52$, λ_2 of the of S−S−F ring RCP is close to zero ($\lambda_2 = 0.0019$) again. Then, the region of $S_2 = +0.11 \rightarrow +0.52$ is the STR and the point $S_1 = +0.27$ is the STS of the F atom transferring for the SSFCl → FSSCl process.

D. Relationship between the Width of the STRs, the Position of the STSs, and the Preference of the Reaction Pathway. Table 4 gives the starting point, the ending point, and the width of the STR as well as the position of STS for each of the titled processes.

Comparing each row of Tables 2 and 4, it can be concluded that for each reaction of SSXY → XSSY (X, Y = F, Cl, Br, I), the width of the STR for the heavier atom transferring is broader than that of the light atom transferring, and the STS of the heavier atom transferring appears later than that of the light atom transferring. It is worthy of noting that in Section III.A

TABLE 4: Width of the Structure Transition Region (STR) and the Position of the Structure Transition States (STS)

	S−S−F three-membered ring		S−S−X three-membered ring	
	STR	STS	STR	STS
SSF$_2$ → FSSF	+0.00→+0.34 (0.34)[a]	+0.13	+0.00→+0.34 (0.34)	+0.13
SSFCl → FSSCl	+0.11→+0.52 (0.41)	+0.27	+0.01→+0.60 (0.59)	+0.29
SSFBr → FSSBr	+0.06→+0.52 (0.46)	+0.28	+0.01→+0.75 (0.74)	+0.36
SSFI → FSSI	+0.16→+0.65 (0.49)	+0.40	+0.01→+0.92 (0.91)	+0.44
	S−S−Cl three-membered ring		**S−S−X three-membered ring**	
	STR	STS	STR	STS
SSFCl → FSSCl	+0.01→+0.60 (0.59)	+0.29	+0.11→+0.52 (0.41)	+0.27
SSCl$_2$ → ClSSCl	+0.07→+0.76 (0.69)	+0.40	+0.07→+0.76 (0.69)	+0.40
SSClBr → ClSSBr	+0.07→+0.76 (0.69)	+0.41	+0.03→+0.87 (0.84)	+0.43
SSClI → ClSSI	+0.14→+0.87 (0.73)	+0.49	+0.06→+1.04 (0.98)	+0.54
	S−S−Br three-membered ring		**S−S−X three-membered ring**	
	STR	STS	STR	STS
SSFBr → FSSBr	+0.01→+0.75 (0.74)	+0.36	+0.06→+0.52 (0.46)	+0.28
SSClBr → ClSSBr	+0.03→+0.87 (0.84)	+0.43	+0.07→+0.76 (0.69)	+0.41
SSBr$_2$ → BrSSBr	+0.01→+0.87 (0.86)	+0.42	+0.01→+0.87 (0.86)	+0.42
SSBrI → BrSSI	+0.12→+1.01 (0.89)	+0.53	+0.06→+1.04 (0.98)	+0.54
	S−S−I three-membered ring		**S−S−X three-membered ring**	
	STR	STS	STR	STS
SSFI → FSSI	+0.01→+0.92 (0.91)	+0.44	+0.16→+0.65 (0.49)	+0.40
SSClI → ClSSI	+0.06→+1.04 (0.98)	+0.54	+0.14→+0.87 (0.73)	+0.49
SSBrI → BrSSI	+0.06→+1.04 (0.98)	+0.54	+0.12→+1.01 (0.89)	+0.53
SSI$_2$ → ISSI	+0.14→+1.16 (1.02)	+0.62	+0.14→+1.16 (1.02)	+0.62

[a] Values in parentheses are the width of the structure transition regions.

we have concluded that the heavier atom transferring is easier than the light atom transferring in each reaction of SSXY → XSSY (X, Y = F, Cl, Br, I). Therefore, for each reaction of SSXY → XSSY (X, Y = F, Cl, Br, I), the broader the STR is, the later the STS appears, and the pathway is easier.

E. Changing Trends of the Width of STR and the Position of the STS with Different Atoms Linked to the Same Three-Membered Ring. For the F atom transferring process in SSFX → TS1 → XSSF (X = F, Cl, Br, I), the S−S−F three-membered ring exists. When different X = F, Cl, Br, and I linked to the same S site of the S−S−F three-membered ring, the width of the ring STR is 0.34, 0.41, 0.46, and 0.49 and the position of the STS is +0.13, +0.27, +0.28, and +0.40, respectively. Therefore, according to the sequence of X = F, Cl, Br, and I linked to the same S site of the S−S−F three-membered ring, the width of the ring STR becomes broader and broader and the position of the STS appears later and later.

From Table 4, for the Cl atom transferring process in SSClX → TS1 → XSSCl, the Br atom transferring process in SSXBr → TS1 → XSSBr, and the I atom transferring process in SSXI → TS1 → XSSI (X = F, Cl, Br, I), the width of the ring STR and respective STS have the same trends.

For a three-membered ring (S−S−F, S−S−Cl, S−S−Br, or S−S−I), different atoms linked to the same S site of the ring are influential to the width of the STR and the position of the STS. The above-discussed S−S−F, S−S−Cl, S−S−Br, and S−S−I ring STR and respective STS have the same trends: according to the sequence of X = F, Cl, Br, and I linked to the same S site of a three-membered ring (S−S−F, S−S−Cl, S−S−Br, or S−S−I), the width of the ring STR becomes broader and broader and the position of the STS appears later and later.

Comparing the columns ΔE(P→TS1) of Table 2 with columns STR and STS of Table 4, it can be concluded that the width of the STR and the position of the STS are related to the energy changes of each group of the SSXY → TS1 → XSSY (X, Y = F, Cl, Br, I) processes.

For the Cl atom transferring of the SSClX → TS1 → XSSCl (X = F, Cl, Br, I) process, ΔE(P→TS1) increases according to the sequence of X = F, Cl, Br, and I, the STR broadens according to the sequence of X = F, Cl, Br, and I, and the position of the STS appears later also according to the sequence of X = F, Cl, Br, and I. The conclusion can be applicable to the F atom transferring of the SSFX → TS1 → XSSF process, Br atom transferring ofthe SSXBr → TS1 → XSSBr process, and I atom transferring of the SSXI → TS1 → XSSI process. In the exothermic reactions, when different X = F, Cl, Br, and I linked to the same S site of a three-membered ring (S−S−F, S−S−Cl, S−S−Br, or S−S−I), the higher the ΔE(P→TS1) is, the broader the ring STR is, and the later the STS appears.

F. Changing Trends of the Width of STR and the Position of STS with Different Three-Membered Rings Linked with the Same Atom. For the X (X = F, Cl, Br, I) atom transferring process in SSFX → TS2 → XSSF, the F atom is linked to the S site of S−S−X three-membered ring. When X = F, Cl, Br, and I, the width of the S−S−X ring STR is 0.34, 0.59, 0.74, and 0.91 and the position of the STS is +0.13, +0.29, +0.36, and +0.44, respectively. Therefore, with the F atom linked to the same S site of the S−S−X three-membered ring, according to the sequence of X = F, Cl, Br, and I, the ring STR becomes broader and broader, and the position of the STS appears later and later.

From Table 3, Table 4, and Supporting Information Table 5, for the X (X = F, Cl, Br, I) atom transferring processes in SSClX → TS2 → XSSCl, SSXBr → TS2 → XSSBr, and SSXI → TS2 → XSSI, the width of the ring STR and respective STS have the same trends.

When the same atom Y linked to different three-membered rings S−S−X (X = F, Cl, Br, I), the influential effect of the different X atom of the S−S−X ring to the STR and respective STS is obvious. With the same atom Y linked to the same S site of the S−S−X three-membered ring, according to the sequence of X = F, Cl, Br, and I, the ring STR becomes broader and broader, and the position of the STS appears later and later.

Comparing the columns Δ*E*(P→TS2) of Table 2 with columns STR and STS of Table 4, it can be concluded that the width of the STR and the position of the STS are related to the energy changes of each group of SSXY → TS2 → XSSY (X, Y = F, Cl, Br, I) processes.

For the X atom transferring process in SSClX → TS2 → XSSCl (X = F, Cl, Br, I), Δ*E*(P→TS2) decreases according to the sequence of X = F, Cl, Br, and I, the STR broadens according to the sequence of X = F, Cl, Br and I, and the position of the STS appears later also according to the sequence of F, Cl, Br, and I. The conclusion can be applicable to the X atom transferring of the processes of SSFX → TS2 → XSSF, SSXBr → TS2 → XSSBr, SSXI → TS2 → XSSI (X = F, Cl, Br, I). In the exothermic reactions, when the same Y atom linked to different three-membered rings S−S−X (X = F, Cl, Br, I), the lower the Δ*E*(P→TS2) is, the broader the ring STR is, and the later the STS appears.

IV. Conclusions

(1) There are two pathways for each process of SSXY to XSSY (X = F, Cl, Br, I): one pathway is via the X atom transferring, and the other one is via the Y atom transferring. For each reaction, the heavier atom transferring is easier than the light atom transferring. The width of the STR of the heavier atom transferring pathway is broader than that of the light atom transferring pathway, and the STS of the heavier atom transferring pathway appears later than that of the light atom transferring pathway. Then, the broader the STR is, the later the STS appears, and the pathway is easier.

(2) When X linked to the same S site of a three-membered ring (S−S−F, S−S−Cl, S−S−Br, or S−S−I), the ring STR becomes broader and the STS appears later according to the sequence of X = F, Cl, Br, and I. And in these cases, for exothermic reactions, the higher the Δ*E*(P→TS1) is, the broader the STR is, and the later the STS appears.

(3) When the same Y atom linked to different three-membered rings S−S−X, the STR becomes broader and the STS appears later according to the sequence of X = F, Cl, Br, and I in the ring. And in these cases, for exothermic reactions, the lower the Δ*E*(P→TS2) is, the broader the STR is, and the later the STS appears.

Acknowledgment. This project was supported by the National Nature Science Foundation of China (20573032), the Nature Science Foundation of Hebei Province (B2006000137), and the Doctoral Foundation of Hebei Normal University (L2005B12).

Supporting Information Available: Table 5 gives topological properties associated with BCPs and RCPs of the SSClX → ClSSX (X = Cl, Br, I) reactions; Table 6 gives topological properties associated with RCPs of the SSXY → XSSY (X, Y = F, Cl, Br, I) reactions; and Figure 4 displays molecular graphs of the SSXY → XSSY (X, Y = F, Cl, Br, I) reactions; the full list of authors of ref 42 is also given. This material is available free of charge via the Internet at http://pubs.acs.org.

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