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Dynamics of endoergic substitution reactions. II. $Br+\{C_2H_2Cl_2\}\rightarrow Cl+\{C_2H_2ClBr\}$

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We have extended the crossed beams studies described in the preceding paper to the reactions of Br atoms with 1,1- and *trans*-dichloroethylene. The shapes of the product translational energy distributions and excitation functions for both reactions support our previous conclusion that Cl elimination from Br–R–Cl collision complexes can compete with Br elimination only in the limit that few vibrational modes of the complex are active in energy redistribution. The substitution cross section for the Br + CH_2CCl_2 reaction is considerably lower than that for the Br + *trans*-CHClCHCl reaction in the collision energy range 15–25 kcal/mol, suggesting that steric effects play a dominant role in determining the relative magnitudes of the cross sections.

I. INTRODUCTION

Gas phase substitution reactions involving unsaturated molecules are generally divided into three steps: addition of the atom/radical to the double bond to form a vibrationally excited collision complex, energy redistribution within the complex and finally emission of another atom/radical. In the 50 years since Kharasch and co-workers discovered the homolytic bromination of alkenes,[1] much experimental and theoretical work has been directed towards understanding the many facets of radical addition reactions.[2] Several factors are believed to influence the kinetics and site specificity of such reactions, including the relative bulk and polarity of the reagents, and the stability of the adduct radical. However, our detailed knowledge of the dynamics and potential energy surfaces of atom/radical + alkene addition reactions has come mainly from molecular beam scattering and chemiluminescence experiments[3] and from *ab initio* quantum chemical calculations.[4]

The energy redistribution and bond fission steps of the substitution process have been the focus of numerous bulk gas phase kinetic studies designed to determine if the unimolecular decomposition of chemically activated radicals is a statistical process. In a series of classic experiments,[5] Rabinovitch and co-workers found that the rates of decomposition of alkyl radicals formed from the addition of H and D atoms to alkenes were in good agreement with the predictions of RRKM theory, implying that energy was randomized among all of the vibrational and internal rotational degrees of freedom of the activated radicals prior to unimolecular decay. Evidence for nonstatistical energy redistribution in chemically activated radicals began to appear in the early 1970's with the work of Rynbrandt and Rabinovitch on the reaction of singlet methylene with hexafluorovinylcyclopropane[6] and with the crossed molecular beam experiments of Lee and co-workers on the reactions of F atoms with a number of unsaturated molecules, F + R–X → X + R–F (where X = H and CH_3).[3(a),7,8]

In these crossed beam studies, the experimental product translational energy distributions $P(E')$ were compared to ones derived from statistical calculations to arrive at a value for the "effective" number of vibrational modes in the collision complexes. The $P(E')$ is sensitive to the distribution of vibration–rotation states along the reaction coordinate at the exit channel transition state but when there is a potential energy barrier in the exit channel, as there is for reactions involving elimination of H and CH_3, repulsive forces between the departing products will channel more energy into translation than would be expected on the basis of this internal state distribution.[9] A more straightforward comparison of experimental and statistical $P(E')$'s can be made for reactions that do not have exit channel barriers, such as substitution reactions involving halogen atom elimination.[10]

The results of crossed beam studies of such reactions are by no means uniform, however. Experiments on F + (1,1-, *cis*-, and *trans*-) $C_2H_2Cl_2\rightarrow Cl+C_2H_2ClF$ by Shobatake, Lee, and Rice[11] yielded $P(E')$ distributions that were consistent with nearly complete energy randomization in the $[C_2H_2Cl_2F]^*$ collision complexes. Cheung, McDonald, and Herschbach[12] obtained statistical $P(E')$ distributions for the reactions Cl + R–Br → Br + RCl for R–Br = C_2H_3Br and 1- and 2-C_3H_5Br, and a nonstatistical distribution for R–Br = 3-C_3H_5Br. Their results were taken as evidence that the vinylic reactions proceed via 1,2 Cl migration whereas the allylic Br + 3-C_3H_5Br reaction involved 1,2 bond migration. However, in higher resolution experiments, Buss *et al.*[13] found that the products of these Cl + R–Br reactions had far more translational energy than would be expected if all of the vibrational modes of the collision complex participated in energy redistribution. Product vibrational energy distributions from chemiluminescence studies of these same reactions were also nonstatistical.[14] Steele *et al.*[15] have recently reinvestigated $Cl+C_2H_3Br\rightarrow Br+C_2H_3Cl$ at a somewhat higher collision energy than Ref. 13. Their results

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are in accord with those of Buss *et al.*[13]

In order to extend our understanding of intramolecular energy transfer in chemically activated radicals and of free radical substitution in general, we undertook crossed molecular beams studies of the endoergic reactions,

$$\mathrm{Br} + \left\{ \begin{array}{c} \mathrm{CH_2CCl_2} \\ trans\text{-}\mathrm{CHClCHCl} \end{array} \right\} \rightarrow \mathrm{Cl} + \left\{ \begin{array}{c} \mathrm{CH_2CClBr} \\ \mathrm{CHClCHBr} \end{array} \right\} \quad \begin{array}{c} (1) \\ (2) \end{array}$$

($\Delta H_0^\circ \simeq 13$ kcal/mol) at four collision energies in the range 15–27 kcal/mol. Our motivations for studying endoergic substitution reactions were outlined at the start of the previous paper. By investigating statistically unfavored channels for a series of isomeric reactions, one can potentially gain a deeper insight into the dynamics of the substitution process at different points along the reaction coordinate. One may begin, for instance, to establish a microscopic basis for familiar rules of chemical kinetics such as the reactivity–selectivity principle, according to which reactions with high threshold energies tend to be more regioselective.[16] Towards this end, we have studied not only the translational energy distribution of the products but the collision energy dependence of the reaction cross sections, or excitation functions, as well.

Our results for the present reactions reinforce our conclusions in the preceding paper[17(a)] regarding the limited extent of intramolecular energy transfer in the bromochlorocyclohexadienyl systems prior to Cl elimination. In fact, these smaller atom–alkene reactions may serve as heuristic models for endoergic substitution in larger molecular systems.

II. EXPERIMENTAL

The apparatus and Br atom source were described in the preceding paper.[17(a)] The Br source stagnation pressures, oven temperature, and nozzle-skimmer configuration were the same as described previously.

The dichloroethylene beam was formed by bubbling 450–500 Torr of He through the cooled (-30 °C) liquid reagent and expanding the resulting mixture through a 0.21 mm diameter nozzle. A conical stainless steel skimmer with an orifice diameter of 0.74 mm was positioned 0.9 cm from the nozzle. The vapor pressures of the reagents at -30 °C are: 40 Torr $\mathrm{CH_2CCl_2}$ (1,1-DCE) and 17 Torr *trans*-CHClCHCl (*t*-DCE). 1,1-DCE was purchased from Aldrich and *t*-DCE from Pfaltz and Bauer.

The collision energy was varied by seeding $\mathrm{Br_2}$ in different rare gases and by heating the DCE beam nozzle with a coaxial heater wire. A list of nozzle temperatures, peak laboratory beam velocities, speed ratios, and most-probable collision energies E_c is given in Table I along with values for the relative reactant flux at each energy, $n_{\mathrm{Br}} n_{\mathrm{DCE}} v_{\mathrm{rel}}$, determined by measuring Br on DCE elastic scattering at a laboratory angle of 16° (see Sec. II of the previous paper[17(a)]).

The 1,1- and 1,2-bromochloroethylene (1,1-, 1,2-BCE) products were monitored at $m/e = 140$ ($\mathrm{C_2H_2Cl^{79}Br}$) but the mass spectrometer resolution was set sufficiently low to allow some of the ^{81}Br containing product to be detected as well. Angular distributions were measured by modulating the DCE beam with a 150 Hz tuning fork chopper. Counting times were 6–18 min per angle. Product time-of-flight spectra were measured using the cross correlation method with a resolution of 10 μs/channel. The flight path from wheel to ionizer was 30.0 cm. Counting times ranged from 0.5–3 h per angle.

A liquid nitrogen cooled copper cold finger was placed against the differential wall inside of the scattering chamber and facing the detector. This improved the signal-to-noise of the 1,1-BCE angular distribution, $E_c = 27$ kcal/mol, by a factor of ≈ 3. The DCE reagents were distilled under dry nitrogen prior to use and stored under rare gas. Nonetheless, at all collision energies there was background at $m/e = 140$ at angles near both beams from elastic and inelastic scattering of impurities in the beams. This was most problematic at the lower collision energies where the product signal was weakest. The background near each beam was measured by substituting a properly diluted beam of Kr for the other beam. The in/elastic scattering angular distribution was then scaled to the product angular distribution and subtract-

TABLE I. Experimental conditions for the Br + DCE reactions.

Reaction	E_c [a]	$n_{\mathrm{Br}} n_{\mathrm{DCE}} v_{\mathrm{rel}}$ [b]	Br		DCE		
			v_{pk} [d]	S[e]	T[c]	v_{pk}	S
Br/He + 1,1-DCE	27	1.00	18.1	6.2	192	12.5	12.8
Br/Ne	21	0.87	15.2	7.4	192		
Br/Ar	17	0.82	12.4	9.5	192		
Br/Ar	15	0.77	*[f]	*	107	10.6	12.6
Br/He + *t*-DCE	27	0.97	*	*	90	13.7	15.0
Br/Ne	23	0.74	*	*	90		
Br/Ar	18	0.64	*	*	90		
Br/Ar	17	0.51	*	*	37	12.2	14.3

[a] Energies are in kcal/mol; collision energies reflect cross section weighting.

[b] Arbitrary units.

[c] Nozzle temperature, °C.

[d] Peak laboratory velocity in units of 10^5 cm/s.

[e] Speed ratio.

[f] * means given above.

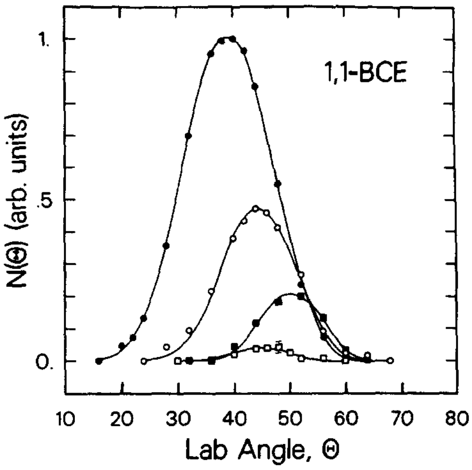

FIG. 1. 1,1-BCE ($m/e = 140$) product angular distribution from reaction (1). ●: $E_c = 27$ kcal/mol; ○: $E_c = 21$ kcal/mol; ■: $E_c = 17$ kcal/mol; □: $E_c = 15$ kcal/mol. Signal is normalized to constant reactant flux but peak of $E_c = 27$ distribution is scaled to unity. Br beam is at 0°. Solid lines are fits to data using c.m. distributions in Figs. 7 and 8 and excitation function in Fig. 10. Center-of-mass angles, in order of decreasing collision energy are: 38°, 44°, 50°, and 44°.

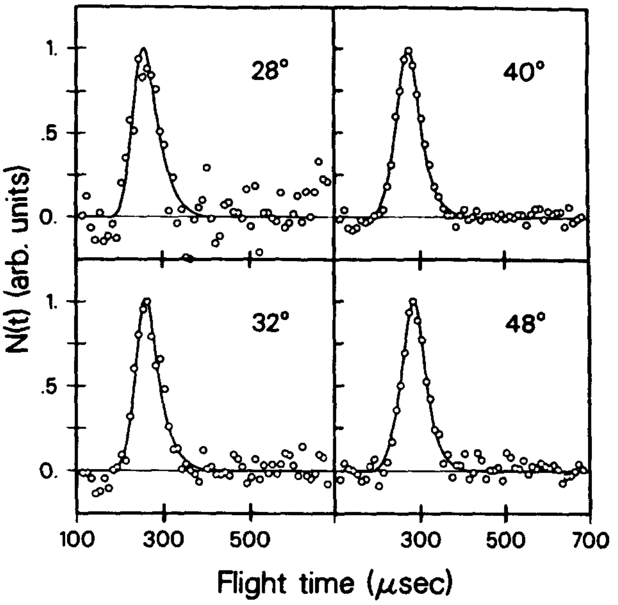

FIG. 3. 1,1-BCE ($m/e = 140$) time-of-flight spectra at $E_c = 27$ kcal/mol. Solid lines represent fits to data using c.m. functions in Figs. 7 and 8 and excitation function in Fig. 10.

ed from it. However, for a few product angular distributions it was not possible to reproduce the slope of the in/elastically scattered signal near one or both beams with the Kr measurements. As a result, we either approximated the nonreactive angular distribution or used a nonreactive distribution obtained at another collision energy which had a similar slope.

III. RESULTS AND ANALYSIS

The BCE product angular distributions and TOF spectra for both reactions are plotted in Figs. 1–6. The peak $m/e = 140$ count rates for the $E_c = 27$ kcal/mol angular distributions were 50 and 320 Hz for reactions (1) and (2), respectively.

The method of analyzing the data was essentially the

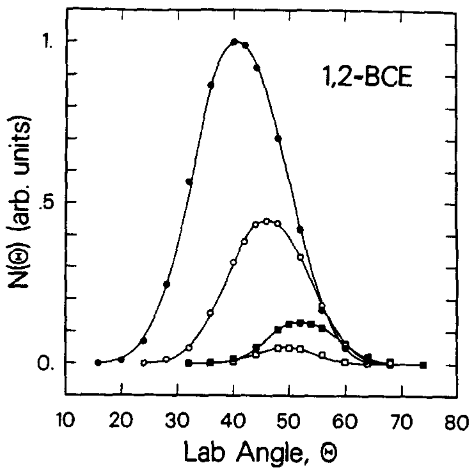

FIG. 2. 1,2-BCE ($m/e = 140$) product angular distribution from reaction (2). ●: $E_c = 27$ kcal/mol; ○: $E_c = 23$ kcal/mol; ■: $E_c = 18$ kcal/mol; □: $E_c = 17$ kcal/mol. See Fig. 1. Excitation function used in fit is plotted in Fig. 10. Center-of-mass angles, in order of decreasing collision energy, are: 42°, 46°, 53°, and 49°.

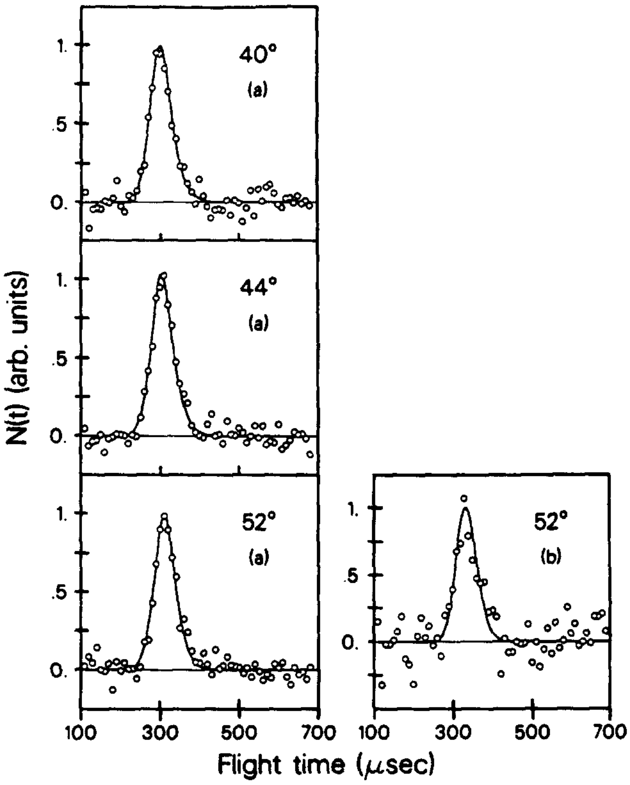

FIG. 4. 1,1-BCE ($m/e = 140$) time-of-flight spectra. (a) $E_c = 21$ kcal/mol; (b) $E_c = 17$. See Fig. 3.

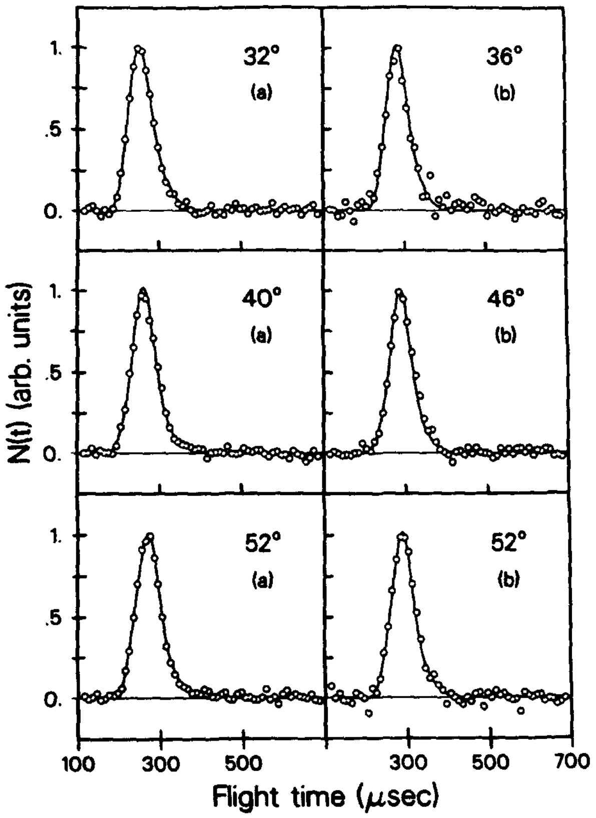

FIG. 5. 1,2-BCE ($m/e = 140$) time-of-flight spectra. (a) $E_c = 27$ kcal/mol; (b) $E_c = 23$. See Fig. 3. Excitation function used in fit is plotted in Fig. 10.

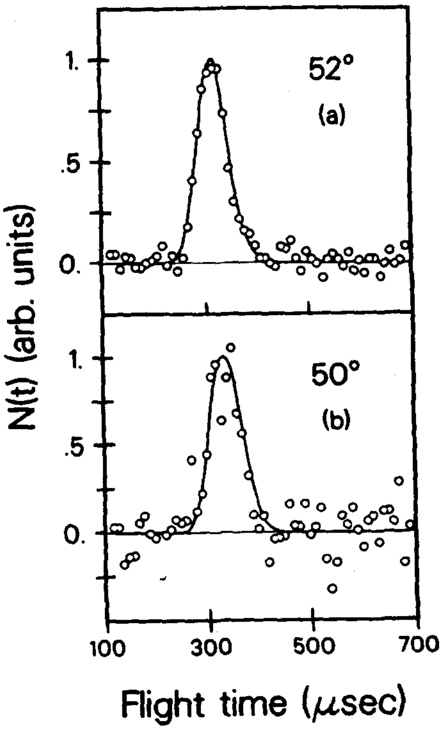

FIG. 6. 1,2-BCE ($m/e = 140$) time-of-flight spectra. (a) $E_c = 18$ kcal/mol; (b) $E_c = 17$. See Fig. 5.

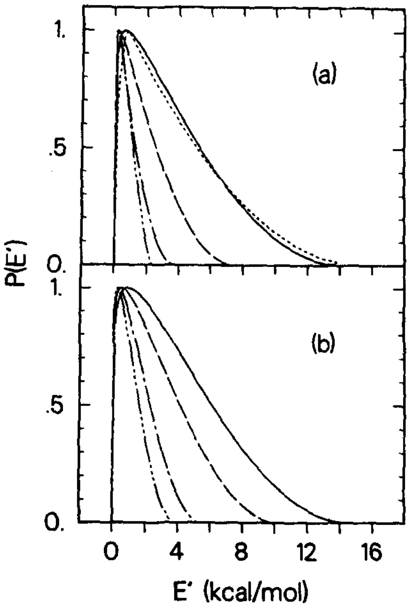

FIG. 7. Center-of-mass frame product translational energy distributions used in fits. (a) Reaction (1): — $E_c = 27$ kcal/mol; – – $E_c = 21$; – – – $E_c = 17$; - - - - - $E_c = 15$; - - - four-mode RRKM-AM calculation. (b) Reaction (2): — $E_c = 27$ kcal/mol; – – $E_c = 23$; – – – $E_c = 18$; - - - - - $E_c = 17$.

same as that described in the previous paper. At the two highest collision energies for each reaction the data were fit with a point form c.m. angular distribution $T(\theta)$. We assumed $\Delta H_0^\circ = 13$ kcal/mol for both reactions (see Sec. IV).

The product translational energy distributions $P(E')$ for both reactions are similar in shape with the 1,2-BCE distributions peaking at slightly higher energies than those for 1,1-BCE (Fig. 7, Table II). $\langle E'/E_{\rm avl}\rangle \simeq 0.3$ for both reactions (where $E_{\rm avl}$ is the total energy available to the products). Note that we obtained approximately the same value of $\langle E'/E_{\rm avl}\rangle$ for the Br + *o*-, *p*-chlorotoluene (CT) reactions.[17] The $P(E')$ for reaction (1) at $E_c = 27$ kcal/mol is in fair agreement with a RRKM-AM $P(E')$ calculated assuming four active vibrational modes with frequencies in the range 250–500 cm^{-1} [18] and a maximum centrifugal barrier, B'_m, of 0.70 kcal/mol [Fig. 7(a)]. The 1,1-BCE angular distribution at this collision energy could not be fit well by a

TABLE II. Fraction of available energy in product translation and $P(E')$ parameters.[a]

Reaction	E_c [b]	$\langle E'/E_{\rm avl}\rangle$ [c]	p	q	B
Br + 1,1-DCE	27	0.26	0.080	2.1	0.08
	21	0.26	0.040	2.1	0.05
	17	0.26	0.040	2.1	0.06
	15	0.32	0.080	1.5	0.06
Br + *t*-DCE	27	0.28	0.12	1.9	0.08
	23	0.28	0.10	1.9	0.05
	18	0.29	0.12	1.9	0.06
	17	0.29	0.13	1.9	0.05

[a] See Ref. 17(a) for functional form of $P(E')$.
[b] kcal/mol.
[c] Fraction for most-probable collision energy.

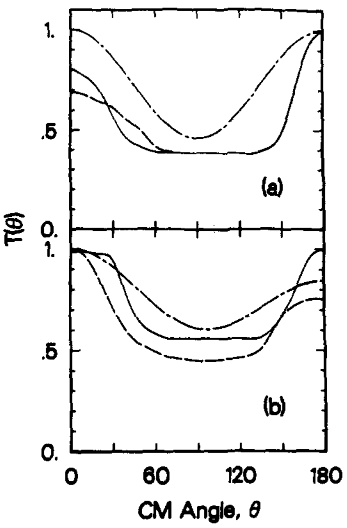

FIG. 8. Center-of-mass frame angular distributions used in fits. (a) 1,1-BCE: — $E_c = 27$ kcal/mol; -- $E_c = 21$; --- $E_c = 17$. $E_c = 15$ distribution is isotropic. (b) 1,2-BCE: — $E_c = 27$ kcal/mol; -- $E_c = 23$; --- $E_c = 18$. $E_c = 17$ distribution is isotropic.

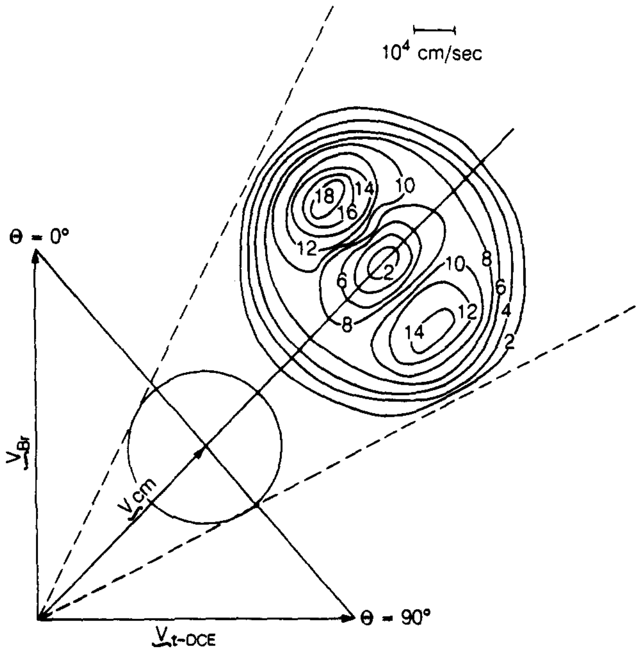

FIG. 9. Center-of-mass frame product flux contour diagram for reaction (2), $E_c = 23$ kcal/mol. Scale is for contours; scale for kinematic (Newton) diagram is half of contour scale.

$P(E')$ in which $q = 4$. The similarity between the falling slopes of the $P(E')$'s for both reactions is particularly interesting considering that the angular dependence of the Cl + BCE interaction potential is likely to be different for the two reactions[10] (see discussion of S_r in Sec. IV).

Although the $T(\theta)$ distributions for reaction (1) [Fig. 8(a)] at $E_c = 27$ and 21 kcal/mol are asymmetric, the areas A under the forward (0°–90°) and backward (90°–180°) parts of each distribution are comparable. At $E_c = 27$ kcal/mol, $R = A(0°–90°)/A(90°–180°) = 0.94$ whereas at $E_c = 21$ kcal/mol, $R = 0.92$. The $E_c = 17$ kcal/mol data could be fit with a symmetric $T(\theta)$ composed of two Legendre polynomials. At this energy, the uncertainties associated with subtracting the $m/e = 140$ background were relatively large. At $E_c = 15$ kcal/mol, the signal-to-noise ratio is very poor as a result of a reduced reaction cross section and no quantitative information is obtainable. We did not collect any TOF data at this collision energy.

Forward scattering of 1,2-BCE from reaction (2) is slightly favored at the three highest experimental collision energies [Fig. 8(b)]. $R = 1.07$, 1.09, and 1.09, at $E_c = 27$, 23, and 18 kcal/mol, respectively. At $E_c = 17$ kcal/mol, we had to guess at the slope of the nonreactive scattering angular distribution near the t-DCE beam so the uncertainties in the product angular distribution (especially for $\Theta > 50°$) are large. This angular distribution could be fit with the same $T(\theta)$ that was used for the $E_c = 18$ kcal/mol data but an isotropic $T(\theta)$ gave a slightly better fit. A c.m. frame flux contour diagram for reaction (2), $E_c = 23$ kcal/mol, is presented in Fig. 9.

The differences between the c.m. angular and translational energy distributions for reactions (1) and (2) can be rationalized by considering the reactant orbital angular momenta **L** for the two reactions. Since the distance between the chlorinated carbon and the center of mass of the molecule is larger in t-DCE than in 1,1-DCE (≈ 0.7 vs ≈ 0.4 Å), we would expect $\mathbf{L}_{(2)} > \mathbf{L}_{(1)}$ and $\tau_{\mathrm{rot}(2)} < \tau_{\mathrm{rot}(1)}$ if the two radicals had about the same moments of inertia, where τ_{rot} is the rotational period of the collision complex. Assuming that the Br atom approaches the chlorinated carbon perpendicular to the plane of the C═C bond, $\mathbf{L}_{(1)} \simeq 70\hbar$ and $\mathbf{L}_{(2)} \simeq 100\hbar$ at $E_c = 27$ kcal/mol. The moments of inertia of the 2-bromo-2,2-dichloroethyl (2,2-BDCE) and 2-bromo-1,2-dichloroethyl (1,2-BDCE) radicals about their rotation axes will be ≈ 350 and ≈ 400 amu Å^2, respectively, assuming that the β- (or 2-) carbon is sp^3 hybridized with C–Br and C–Cl bond lengths of 2.0 and 1.8 Å and that the C$_\alpha$–Cl and C$_\alpha$–H bonds lie in the original C═C plane. Therefore, neglecting the small rotational angular momenta of the reactants, $\tau_{\mathrm{rot}} \approx 5$ ps for 2,2-BDCE and ≈ 4 ps for 1,2-BDCE. If the lifetimes of the BDCE radicals are comparable to each other, we might expect slightly more forward scattering from reaction (2). The higher peak energies of the $P(E')$'s for (2), which indicate that $\mathbf{L}'_{(2)} > \mathbf{L}'_{(1)}$ (where the prime refers to products), also accord with $\mathbf{L}_{(2)}$ being greater than $\mathbf{L}_{(1)}$.

The approximate forward–backward symmetry in $T(\theta)$ for both of these reactions contrasts with the marked asymmetry in $T(\theta)$ for the Br + chlorotoluene (CT) reactions. Unlike Br + CT→BCMC, which is endoergic by ≈ 2 kcal/mol, Br addition to DCE is exoergic by ≈ 8 kcal/mol (see Sec. IV). This difference in exoergicity might explain the apparently larger values of τ/τ_{rot} for BDCE (where τ is the lifetime of the complex). We have calculated RRKM lifetimes for the bromo-dichloroethyl collision complex using approximate frequencies for the 15 vibrational modes of the energized radical and the 14 modes of the activated complex.[20,46] With $E_0 = 8$ and 21 kcal/mol for the Br and Cl elimination channels, we obtain lifetimes τ_{RRKM} of ≈ 0.5 and ≈ 0.3 ps for 2,2-BDCE and 1,2-BDCE, respectively, at $E_c = 27$ kcal/mol. As we found for BCMC,[17(b)] the calculated rotational periods for the BDCE complexes are considerably longer than the RRKM lifetimes. However, $\tau_{\text{rot}}/\tau_{\text{RRKM}} \approx 10$ for BDCE whereas the same ratio is ≈ 250 for BCMC. Thus, the near symmetry of the product angular distributions for the present reactions is most likely due to the longer lifetimes of the reaction intermediates.

The curvatures of the $T(\theta)$ distributions from $\theta = 0°$–$40°$ and $140°$–$180°$ have a pronounced effect on the widths of the calculated TOF spectra. The more suddenly $T(\theta)$ changes over a range of c.m. angles, the narrower the TOF spectra at LAB angles in that range will be. In order for the calculated and experimental TOF spectra to agree in reaction 1, $E_c = 27$ and 21 kcal/mol, and reaction (2), $E_c = 27$ kcal/mol, $T(\theta)$ must rise more steeply at wide (140°–180°) than at small (0°–40°) c.m. scattering angles. The reverse is true for reaction (2) at $E_c = 23$ kcal/mol.

The data at the highest collision energies might actually reflect a narrowing of the product translational energy distribution at wider angles. It is possible that, as a consequence of angular momentum conservation, the c.m. product translational energy and scattering angle distributions are coupled. When the initial reactant rotational angular momentum is negligible and **L** and **L**′ are of comparable magnitude, high **L** collisions will contribute most strongly to scattering at 0° and 180° in a reaction that proceeds through a long-lived complex. Part of the rotational energy of the complex at its exit transition state will go into product translation so the $P(E')$ distributions for scattering near 0° and 180° would be expected to peak at higher energies.[13] When the lifetime of the collision complex is comparable to or shorter than its rotational period, an asymmetry in the θ–**L** coupling might arise, with small **L** (long τ_{rot}) collisions dominating scattering at wide angles and large **L** (small τ_{rot}) contributing most strongly to scattering at small angles. In such a case, we would expect the translational energy distributions for backward scattered products to peak at lower energies than those for forward scattered products.

A comparison of the reduced masses and the most-probable relative velocities of the reactants and products for both reactions indicates that, in all cases, the average exit impact parameter would have to be $\approx$3–4 times larger than the average entrance impact parameter for $\mathbf{L}' = \mathbf{L}$. This is certainly unlikely; some fraction of **L** will be carried away as rotational angular momentum of the products **J**′. However, the relatively strong peaking in $T(\theta)$ at 0° and 180°[19] and the fact that the peak energies of the $P(E')$'s, E'_{pk}, which are proportional to $|\mathbf{L}'|^2$, increase with **L** [i.e., $E'_{\text{pk}} \propto E_c$, and $E'_{\text{pk}}(2) > E'_{\text{pk}}(1)$] indicate that **L**′ is strongly correlated to **L**.

The excitation functions S_r used to reproduce the relative intensities of the LAB angular distributions are plotted in Fig. 10. The shaded regions indicate the uncertainties in S_r above the highest most-probable collision energies. The thresholds were set at 13.5 kcal/mol since this helped in obtaining the proper scaling factor for the 1,1-BCE, $E_c = 15$ kcal/mol, angular distribution. The poor signal-to-noise of the low energy angular distributions and relatively wide spread in collision energy prevents us from determining the thresholds to these reactions accurately. (Note that at $E_c = 15$ kcal/mol, a large fraction of the Br + 1,1-DCE collisions have insufficient energy to overcome the endoergicity to Cl substitution.)

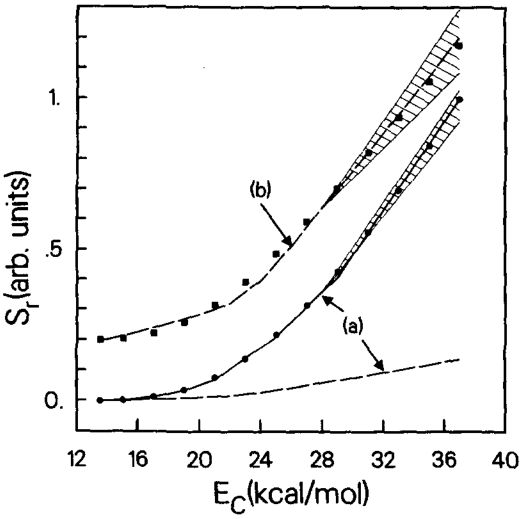

FIG. 10. Excitation functions for reactions (1) (– –) and (2) (—). (a) Curves depict the correct relative magnitudes of the excitation functions; (b) excitation function for reaction (1) enlarged and offset arbitrarily. ■: six-mode RRKM branching ratio calculation; ●: eight-mode RRKM branching ratio calculation. Shaded regions indicate uncertainty in S_r above the highest most probable E_c.

As discussed in the previous paper, if the Br addition cross section is assumed to be independent of collision energy, the experimental excitation functions can be compared with RRKM calculations of the product branching ratios. S_r(1,2-BCE) is found to agree well with an eight-mode ($\nu = 200$–$800\ \text{cm}^{-1}$; $E_0 = 8$ and 21.5 kcal/mol) RRKM branching ratio curve S_{RRKM} whereas S_r(1,1-BCE) is in qualitative agreement with a six-mode RRKM function ($\nu = 200$–$650\ \text{cm}^{-1}$) (Fig. 10).

We tried to determine the extent of Br elimination, $[\text{BDCE}]^* \rightarrow \text{Br} + \text{DCE}$, in both reactions by measuring TOF spectra at $m/e = 79$ and $m/e = 96$ near the center-of-mass angle at several collision energies. At all energies, however, in/elastic scattering of the reactants dominated the spectra and slow Br and DCE from the decay of the collision complex was not observable.

1,1-DCE has C–C–Cl (B_1) and Cl–C–Cl (A_1) bending modes at 375 and 299 cm^{-1}; *t*-DCE has C–C–Cl bending modes of A_g and B_u symmetry at 349 and 250 cm^{-1}.[20] Assuming no relaxation of these vibrations during supersonic expansion, the fraction of DCE molecules in the beam that has at least one quantum of C–C–Cl or Cl–C–Cl bend ($f_{v>0}$) is $\approx 50\%$ at a nozzle temperature of 30 °C. For each reaction, $f_{v>0}$ changes by $\approx 10\%$ over the experimental nozzle temperature range (Table I). It is possible that energy in these bending vibrations can couple into the C–Cl reaction coordinate and thereby affect our measurements of the translational energy dependence of the substitution cross sections near threshold. Manning *et al.*[21] found no enhancement in the rate constant for the reaction(s) O + C_2H_4

$\rightarrow$[products] with vibrationally excited C_2H_4, but their analysis is based upon a complicated kinetic scheme for excitation and deactivation of the reagent involving rate constants of unknown magnitude. Also, Hase *et al.*[22] concluded from classical trajectory calculations that two quanta in the CH_2 wagging mode of ethylene has little effect on the $H + C_2H_4$ addition cross section.

IV. DISCUSSION

Reactions (1) and (2) are not likely to differ much in endoergicity. Rosenstock *et al.*[23] report the heats of formation (ΔH°_{f0}) of 1,1-DCE and *t*-DCE to be 2.01 and 2.76 kcal/mol, respectively. The heats of formation of the C_2H_2ClBr isomers are unknown. However, $\Delta H^\circ_0 = 12.4$ kcal/mol for the reaction $Br + C_2H_3Cl \rightarrow C_2H_3Br + Cl$.[23,24] We assume that the C–X (X = Br, Cl) bond dissociation energies in the isomers of $C_2H_2Cl_2$ and C_2H_2ClBr differ by less than 1 kcal/mol from those in C_2H_3Br and C_2H_3Cl and take $\Delta H^\circ_0 = 13$ kcal/mol for reactions (1) and (2).

The activation energies for halogen atom addition to alkenes are known to be very small or zero.[25] From experiments on the photochemical bromination of *t*-DCE, Schumacher[26] concluded that there is no activation energy to the reaction Br + *t*-DCE → 1,2-BDCE. The activation energies for Cl addition to ethylene and its chlorinated derivatives are uniformly ≈ 0 kcal/mol.[27]

As mentioned in the previous paper, the thermochemistry of Br addition to unsaturated molecules is not well understood. Benson and O'Neal[28] report $\Delta H^\circ_{298} = -8.8$ kcal/mol for the reaction $Br + C_2H_4 \rightarrow C_2H_4Br$. With $\Delta H^\circ_0 = 12.4$ kcal/mol for $Br + C_2H_3Cl \rightarrow Cl + C_2H_3Br$ and D°_0 (C–Cl) = 19.3 kcal/mol for $CH_2CHClBr$ radical,[4(c),23,29] $\Delta H^\circ_0 = -6.9$ kcal/mol for $Br + C_2H_3Cl \rightarrow CH_2CHClBr$. The C=C bond dissociation energies in $C_2H_2Cl_2$ and C_2H_4 ($D^\circ_{298} \simeq 143$ vs 172 kcal/mol[30]) do not differ enough for $Br + C_2H_2Cl_2 \rightarrow C_2H_2Cl_2Br$ to be significantly more exoergic than $Br + C_2H_4 \rightarrow C_2H_4Br$. [Br addition to CH_2CF_2, in which D°_{298}(C=C) = 130 kcal/mol,[30] is just ≈ 4 kcal/mol more exoergic than Br addition to C_2H_4.[31]] Indeed, the reactions (a) $Cl + C_2H_4 \rightarrow C_2H_4Cl$ and (b) $Cl + CHClCHCl \rightarrow CHClCHCl_2$ have the same exothermicity within experimental error ($\Delta H^\circ_{298} = -20.2$[4(c),23] vs -19.7 ± 3[32] kcal/mol). There is evidence that CH_2CCl_3 radical is an unstable species which undergoes rapid 1,2 Cl migration.[33,34] But, using group additivity, Franklin and Huybrechts[32] calculate $\Delta H^\circ_{298} = -15.3$ kcal/mol for $Cl + CH_2CCl_2 \rightarrow CH_2CCl_3$, which agrees with ΔH°_{298} for (b) within the stated uncertainties. Thus, the C–Br bond energies in 2,2- and 1,2-BDCE may not differ greatly from that in CH_2CH_2Br.

As for the Br + chlorotoluene reactions, the $P(E')$ distributions and excitation functions for the Br + DCE reactions imply that only a limited number of vibrational modes in the energized radicals participate in energy redistribution prior to Cl elimination. Our analysis suggests that the fraction of active modes is roughly the same in 2,2- and 1,2-BDCE. This is noteworthy considering that 2,2-BDCE has more low frequency Cl–C–X (X = Cl, Br) bending modes ($\nu = 200$–$300\ cm^{-1}$) than 1,2-BDCE and that these modes are principally associated with the carbon atom that was attacked. It is thus possible that a similar subset of modes is excited in both reactions. Most striking, however, is that the number of active modes remains approximately the same for both the Br + DCE and Br + CT reactions. This finding reinforces our earlier conclusion that substitution of Cl for Br in Br + CT is a localized, or quasidirect, process and suggests that endoergic atom–alkene substitution reactions can serve as models for endoergic atom–aromatic molecule reactions.

The crossed beam studies of the exoergic substitution reactions F + (1,1-, *trans*-) $C_2H_2Cl_2 \rightarrow Cl + C_2H_2ClF$ ($\Delta H^\circ \simeq -30$ kcal/mol; $E_c = 2.5$ kcal/mol)[11] yielded c.m. frame C_2H_2ClF angular distributions for both reactions that were isotropic and product translational energy distributions that were consistent with collision complexes in which nearly all of the vibrational modes participated in energy redistribution. Whereas $\langle E'/E_{\rm avl}\rangle \simeq 0.16$ for these reactions, earlier experiments gave $\langle E'/E_{\rm avl}\rangle \simeq 0.11$ for the roughly isoenergetic $F + C_6H_5Cl \rightarrow Cl + C_6H_5F$ reaction.[35] This difference in average product translational energy was attributed to a smaller number of active vibrational modes in the $[C_2H_2Cl_2F]^*$ collision complexes. However, the *fraction* of active modes in these complexes was found to be larger than that in $[C_6H_5ClF]^*$.

Although the additional C_β–Cl bond in 2,2-BDCE may not appreciably enhance intramolecular energy transfer, the presence of this bond in 1,1-DCE appears to have a pronounced effect on the magnitude of the substitution cross section for reaction 1. At $E_c = 27$ kcal/mol, $S_r(1,1)$ is ≈ 6 times smaller than $S_r(1,2)$. (Note that although *t*-DCE has two identical carbon atoms available for Br attack, the reaction path degeneracy for Cl elimination from 2,2-BDCE is twice that for 1,2-BDCE.) Thus, if the two BDCE isomers have roughly the same number of active modes, the cross section for Br addition, $\sigma_{\rm add}$, to 1,1-DCE must be lower than that to *t*-DCE.

The original theory of anti-Markownikoff addition, formulated to explain the kinetics of HBr addition to alkenes in the presence of peroxides or ultraviolet light, postulated that the preferred site of radical attack is determined by the relative stabilities of the two possible adducts.[36] Thus, addition to the least substituted carbon atom would be favored since the resulting adduct radical will be resonance stabilized. There is, however, a paucity of data on the heats of formation of halogenated alkyl radicals so it is difficult to argue on thermodynamic grounds about preferred pathways for addition. As mentioned above, the experimental evidence for the chlorinated ethyl radicals indicates that $D^\circ(C_\beta\text{–}Cl)$ is relatively independent of the extent of chlorination.[32] Johari *et al.*[37] have shown that the rate of addition of CCl_3 to the CF_2 end of $CHClCF_2$ is 25 times greater than the rate of addition to the CHCl end, a result that is inconsistent with the notion that resonance stabilization of the adduct determines the preferred position of attack. Indeed, Tedder and Walton have argued convincingly that the orientation of many radical addition reactions can be correlated straightforwardly with the bulk of the radical and the substituents on the alkene as well as with the relative electronegativities of the reagents.[2(a),2(c)]

Experiments on radical addition to alkenes indicate that Cl substituents strongly influence rate constants for addition. Chiltz *et al.*[27] report values of log A for the reactions $Cl + C_2H_4 \rightarrow C_2H_4Cl$ and $Cl + C_2Cl_4 \rightarrow C_2C_5$ of 10.2 and 9.4, respectively. Since these reactions have no activation energy, this is equivalent to a sixfold difference in rate constant. Bertrand *et al.*[38] studied the products of the Cl-photosensitized oxidation of C_2HCl_3 and isomers of $C_2H_2Cl_4$ and concluded that the rate constant for Cl addition to the less chlorinated carbon atom in C_2HCl_3 is at least eight times greater than that for addition to the more chlorinated carbon. Johari *et al.*[37] have found that CCl_3 adds ≈ 300 times more readily to the CHCl end of $CHCl = CCl_2$ than to the CCl_2 end. The simplest explanation of these data and our results for Br + 1,1-DCE is that Cl substituents hinder approach of the attacking atom and thereby reduce the probability of addition.

The shapes of the excitation functions suggest that the two BDCE complexes have about the same number of active modes but if σ_{add} were dependent on collision energy, the curvature of S_r would not simply reflect the energy dependence of the statistical branching ratio and the ratio $\sigma_{\text{add}}(1,1)/\sigma_{\text{add}}(1,2)$ could not be extracted from the magnitudes of the S_r.[17] According to the classical RRK theory,[39]

$$\eta_{\text{Cl}}/(\eta_{\text{Cl}} + \eta_{\text{Br}}) \propto [(\epsilon^{\dagger}_{\text{Br}}/\epsilon^{\dagger}_{\text{Cl}})^{s-1} + 1]^{-1}, \qquad (3)$$

(where η_X is the probability of X elimination, $\epsilon^{\dagger}_X$ is the excess energy at the critical configuration, $E^* - E_0$, and s is the number of active vibrational modes) so, for two reactions with the same energetics, the one with the larger number of modes involved in energy sharing should have the lower substitution cross section and the steeper excitation function. Thus, if the lower cross section for reaction (1) resulted from 2,2-BDCE having more active modes, $\sigma_{\text{add}}(1,1)/\sigma_{\text{add}}(1,2)$ would have to decrease with increasing collision energy in order for the slopes of the two excitation functions to be similar.

Based on our discussion of the Br + CT excitation functions,[17] however, the cross section for Br addition to the sterically hindered 1-carbon of 1,1-DCE would be more likely to show a positive than a negative energy dependence. Likewise, we would not expect $\sigma_{\text{add}}(1,2)$ to increase more strongly with collision energy than $\sigma_{\text{add}}(1,1)$. So, it does not appear reasonable to invoke differences in the number of active modes along with an energy dependent addition cross section to explain the lower substitution cross section for reaction (1). It is more likely that steric effects cause $\sigma_{\text{add}}(1,1) < \sigma_{\text{add}}(1,2)$ at all collision energies.

In the crossed beam study of the F + 1,1- and *t*-DCE reactions, Shobatake *et al.*[11] found that $S_r(1,1)$ was only slightly ($\approx 20\%$) smaller than $S_r(1,2)$. (The substitution cross section for *cis*-DCE was comparable to that for 1,1-DCE.) Indeed, we would not expect F atom addition reactions to be very site selective considering their large exoergicity ($-\Delta H^{\circ}_0 = 40$–50 kcal/mol). In the Br + DCE reactions at elevated collision energies, where Br addition is much less exoergic and long range attractive forces between the reactants are not significant, subtle differences among the isomeric potential energy surfaces (i.e., in the angular dependence of the Br–DCE interaction potential and in the slope of the potential energy surface along the reaction coordinate)[17] will manifest themselves more strongly in the reaction cross sections. Thus, steric effects are more likely to dominate in Br addition reactions.

A. The question of migration

Given the evidence that atoms and radicals add preferentially to the less substituted end of chlorinated derivatives of ethylene, it is worth considering the likelihood that 1,1-dichloro-2-bromoethyl radicals formed from Br addition to the CH_2 end of 1,1-DCE rearrange via Br or Cl migration and subsequently decompose to give Cl + 1,1-BCE. There is a large body of data on the stereo-specific addition of HBr to alkenes that has been interpreted as evidence for 1,2 bridged bromoalkyl radicals.[40] ESR experiments on 2-chloroethyl radical[41] and 2-bromo-tert-butyl radical $[BrCH_2\dot{C}(CH_3)_2]$[42] suggest that these species do exist in preferred conformations, the former with a planar radical center and the C–Cl bond eclipsing the unpaired electron orbital and the latter with a nonplanar radical center and the C–Br bond *gauche* staggered with respect to the unpaired orbital. (The bromoethyl radical has not been observed by ESR spectroscopy.[43]) However, no evidence for symmetrical bridging of the halogen atom was found in these studies. *Ab initio* calculations on 2-chloroethyl radical predict that the chlorinated carbon atom is tetrahedral[4(c),44] and that the symmetrically bridged structure is unstable with respect to dissociation to $Cl + C_2H_4$.[44]

In a study of the $Cl + C_2H_3Br$ reaction using radioactive ^{38}Cl atoms and HI as a radical scavenger, Iyer and Rowland[45] found that the yields of (I) $CH_2^{38}ClCH_2Br$ (the product of the reaction of the stabilized adduct $CH_2^{38}ClCHBr$ with HI) and (II) $CH_2 = CH^{38}Cl$ were both pressure dependent, the dominant product being (I) at higher pressures and (II) at lower pressures. The yield of $CH_3CH^{38}ClBr$ (from $CH_2CH^{38}ClBr$) was always less than 0.1%. They rule out a mechanism in which unimolecular decomposition of $CH_2CH^{38}ClBr$ through Br elimination is much more rapid than its collisional stabilization and explain their results by invoking halogen atom migration (either Cl or Br) to give the substitution product (II).

We see no reason why Br or Cl migration should be important in the present reactions. The reduced substitution cross section observed for 1,1-DCE is straightforwardly explained by a lower probability for Br addition to the chlorinated carbon. Although the rotational barrier to 2→1 Br migration in 2-bromo-1,1-dichloroethyl radical is only ≈ 3 kcal/mol at $E_c = 27$ kcal/mol, it seems unlikely that a migrating Br atom would be as effective at displacing a Cl atom as one that directly attacks the 1-carbon of 1,1-DCE. The translational energy distribution and excitation function for reaction (1) both suggest that fewer vibrational degrees of freedom are active in the endoergic substitution process than one might expect if Br had to migrate to displace Cl. Also, the similarity between the $P(E')$'s and excitation functions for reactions (1) and (2) argues that the dynamics of the two reactions (after the initial addition step) are rather similar.

V. CONCLUSIONS

Our results for the Br + DCE→Cl + BCE reactions are consistent with the model described in the previous paper whereby endoergic substitution occurs most readily when it is a quasidirect process. Exoergic Br elimination is always the statistically favored mode of decay of the BDCE collision complex but Cl elimination becomes a competitive channel when vibrational energy redistribution is limited. Although the slopes of the $P(E')$'s and excitation functions for both reactions are comparable, $S_r(1,1)$ is substantially lower than $S_r(1,2)$ at most collision energies, suggesting that steric effects play a dominant role in determining the relative magnitudes of the substitution cross sections. Such effects are likely to be observable only in reactions that have large energetic thresholds. Finally, the similarity between the "effective" number of vibrational modes in the Br + DCE and Br + CT reactions offers the intriguing possibility that endoergic aromatic substitution reactions can be modeled by analogous atom–alkene reactions.

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