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Dynamics of Endoergic Aromatic Substitution Reactions

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ABSTRACT

The endoergic substitution reactions $\text{Br} + \text{o-,m-,p-CH}_3\text{C}_6\text{H}_4\text{Cl} \rightarrow \text{o-,m-,p-CH}_3\text{C}_6\text{H}_4\text{Br} + \text{Cl}$ ($\Delta H_0^\circ \approx 15 \text{ kcal/mol}$) have been studied using the crossed beams method in the collision energy range 20–30 kcal/mol. o-chlorotoluene was found to be more reactive than p-chlorotoluene at the highest collision energy but the reverse was true below 25 kcal/mol. No reaction was observed for the meta isomer. An explanation for the lower reactivity of m-chlorotoluene is offered in terms of possible features of the potential energy surface.

In all of the reactions observed, the products are forward scattered, indicating that the majority of collision complexes survive for less than one rotational period. This is understandable in light of the $\sim 2 \text{ kcal/mol}$ endoergicity to Br addition that results from the loss in resonance stabilization energy. Little of the energy available to the products of these reactions is channeled into translation. The experimental product translational energy distributions and excitation functions suggest that, in those complexes that decompose through Cl elimination, only a few vibrational degrees of freedom in the vicinity of the collision are involved in energy redistribution.

INTRODUCTION

Although homolytic, or free-radical, aromatic substitution reactions have been the subject of many kinetic studies [1,2,3], their detailed dynamics in both the liquid and gas phases are only partially understood. In the gas phase, they proceed by addition of an atom or radical to an aromatic ring to form an activated cyclohexadienyl radical which subsequently decomposes through emission of another atom/radical. Questions relating to the dynamics of atomic addition to the ring, the features of the potential energy surface along the reaction coordinate, the extent of intramolecular vibrational energy redistribution prior to unimolecular decomposition, and the relative importance of all of these factors in determining the energy dependence of the reactive cross section can all be addressed by the method of crossed beams scattering.

Endoergic substitution reactions are particularly intriguing since cleavage of the stronger bond is not the statistically favored mode of decay of the chemically activated radical. Thus, observing the endoergic channel may offer some insight into factors other than the amount of phase space available to the activated radical and products that determine the course of the reaction. In the case of aromatic substitution reactions, one may, in addition, observe the effects of substituents on the reactivity of different sites on the aromatic ring. Since these effects are related to the energetics of adduct formation, they should be most pronounced in those reactions where the reagent atom/radical bonds weakly to the ring. In this respect Br is an ideal reagent.

We have carried out a crossed molecular beam study of the endoergic substitution reactions, $\text{Br} + \text{o-,m-,p-CH}_3\text{C}_6\text{H}_5\text{Cl} \rightarrow \text{Cl} + \text{o-,m-,p-CH}_3\text{C}_6\text{H}_5\text{Br}$ ($\Delta H_0^\circ = 15 \text{ kcal/mol}$, fig 1) in the collision energy range of 20–30 kcal/mol. The results of these experiments shed new light on the role of substituents in controlling the orientation of aromatic substitution and on the dynamics of these reactions in general.

EXPERIMENTAL

The crossed beam apparatus used in these experiments has been described previously [4,5]. Two seeded, differentially pumped reagent beams cross at 90° in a vacuum chamber held at approximately 10^{-7} torr. The products are detected with a triply differentially pumped mass spectrometric detector that rotates in the plane of the two beams.

The bromine atom beam was generated by passing a mixture of Br_2 in rare gas through a resistively heated high density graphite oven designed in this laboratory by Valentini et. al. [6]. The Br_2 /rare gas mixture is created by bubbling approximately 700 torr of He, Ne, or Ar through liquid bromine (reagent grade Fischer and Mallinckrodt) at 0°C ($p_{\text{Br}_2} \approx 60$ torr). The oven had a nozzle diameter of 0.14 mm and was run at approximately 1380°C . A conical graphite skimmer having an orifice diameter of 0.10 cm was positioned 0.76 cm from the nozzle. Ninety percent of the Br_2 dissociated into Br atoms, as determined from a direct measurement of Br/Br_2 in the beam.

The secondary molecular beam was formed by bubbling 450 torr of He through chlorotoluene heated to 60°C in a bath and expanding the mixture through a 0.21 mm diameter aperture nozzle. A stainless steel skimmer with an orifice diameter of 0.66 mm was positioned 0.89 cm from the nozzle. o- and p-chlorotoluene (o-, p-CT) were purchased from MCB and m-CT from Aldrich. The source and feed line were heated with coaxial heating wire to a temperature of 200°C. All of the compounds were used without further purification, except for the p-CT which was distilled on a spinning band column.

In order to reduce the background at the product mass, a liquid nitrogen cooled copper cold finger was placed against the differential wall inside of the scattering chamber so that the detector would always face a cold surface during the angular scans. Product angular distributions were measured by modulating the CT beam with a 150 Hz tuning fork chopper and collecting data with the beam on and off using a dual channel scaler. Data was collected for approximately six minutes per angle.

In order to compute relative cross sections for a given reaction at different collision energies, we scaled the product number density by the reactant flux, which is proportional to $n_{Br} n_{CT} |v_{rel}|$, where n_i = number density of beam i and v_{rel} = relative velocity. Since the wide angle Br elastic scattering cross section does not change drastically as a function of energy, measuring Br on CT elastic scattering allows us to measure changes in this quantity. During each scan, the m/e 79 signal was monitored at three different LAB angles. The angles were all beyond the cutoff angle for elastic scattering of Br on He so the Br^+ signal observed

was from Br scattering on CT. The contribution of undissociated Br₂ to the m/e 79 signal was very small and was neglected. Relative values for $n_{\text{Br}} n_{\text{CT}} / n_{\text{e}}$ derived from the Br elastic number density at angle of 16° are given in Table 1.

The velocities of the reactant beams were measured using the time-of-flight (TOF) technique. A 256 channel scaler interfaced with an LSI-11 computer accumulated the data. No TOF measurement was made for the m-CT beam, but its velocity should be identical to that of o-CT since both have the same vapor pressure (22 torr; p-CT= 21 torr) at 60° C. The peak beam velocities (in units of 10⁵ cm/s), and speed ratios, S, are: Br/He: 1.85, S=6.1; Br/Ne: 1.55, S=6.9; Br/Ar: 1.29, S=8.4; o-CT/He: 1.33, S=11.3; p-CT/He: 1.35, S=11.8. Product TOF were measured using the cross-correlation method [5]. Counting times were approximately 1 hr per angle.

RESULTS AND ANALYSIS

The ortho- and para-bromotoluene (BT) substitution product was detected at m/e 170 (⁷⁹Br), however the quadrupole mass spectrometer resolution was set sufficiently low to allow some of the ⁸¹Br product to be detected as well. The product angular distributions are shown in fig 2. Elastic scattering of impurity in the p-CT beam contributed to background at m/e 170 near that beam. This was most problematic at a collision energy, E_c, of 21.4 kcal/mol where the product signal level was lowest. At this energy the the elastic scattering background was measured by substituting a properly diluted beam of Kr in Ar for the Br in Ar beam. It was then scaled to the

product angular distribution at 74° and subtracted from it. At the peak of the $E_c=31.0$ kcal/mol o-BT angular distribution, the product count rate was 20 Hz. The angular distributions reveal that, at all energies, the o- and p- product is slightly forward scattered with respect to the center-of-mass angle for the collision. Remarkably, no BT product was detected for the reaction $\text{Br} + \text{m-CT}$ at a collision energy as high as 31.0 kcal/mol. TOF spectra of p-BT, $E_c=31.5, 21.4$ kcal/mol, and o-BT, $E_c=25.3, 20.9$ kcal/mol, are presented in figs. 3 and 4. At each collision energy, the TOF spectra at different angles have peak flight times close to that of the velocity of the center-of-mass (fig. 7), indicating that little energy is channeled into translation.

The product angular distributions and TOF spectra were fit using a forward convolution program [7] that starts with a separable form for the CM reference frame product flux distribution, $I_{\text{CM}}(\theta, E') = T(\theta)P(E')$, and generates LAB frame angular distributions and TOF spectra suitably averaged over the spread in relative velocities. $T(\theta)$, the CM frame angular distribution, is taken to be a sum of three Legendre polynomials whose coefficients are varied to optimize the fit. A RRK functional form is used for $P(E')$, the CM frame product translational energy distribution: $P(E') = (E' - B)^p (E_{\text{tot}} - E')^q$, where B is related to any barrier in the exit channel and E_{tot} is the total energy available to the products ($E_c - \Delta H_0^\circ$). ΔH_0° was taken to be 15 kcal/mol (see Discussion). The parameters p , q , and B were optimized to give the best fit to the data.

For a given experiment, the spread in beam velocities and intersection angles gives rise to a spread in relative velocities and hence in collision energies. $\Delta E_C/E_C(\text{FWHM}) \sim 30\%$ for the reactions with Br seeded in He and $\sim 25\%$ for the reactions with Br seeded in Ne and Ar. Each beam velocity and intersection angle permutation corresponds to a different kinematic configuration (Newton diagram) over which the calculated angular distribution and TOF fits must be averaged. The collision energies corresponding to the most probable kinematic configurations are listed in table 1. Since, for an endoergic reaction, the maximum translational energy of the products will depend strongly on E_C , a $P(E')$ with a unique value of E_{tot} was used for each kinematic configuration in the analysis. Also, since the cross section is found to depend on collision energy, each kinematic configuration was weighted according to E_C . Because of the large spread in E_C , it was necessary to extrapolate the excitation function used in the weighting routine beyond the most probable experimental collision energies. This was done by taking the cross section at $E_C=15$ kcal/mol to be 0.0 and extrapolating linearly beyond the highest energy. The high energy extrapolation has a marked affect on the fits to the $E_C=31$ kcal/mol data, since it is used to determine the most probable collision energy and center-of-mass angle. Linear extrapolation, however, appears to be the most unbiased approach to this problem.

Although the data offer some latitude with regard to the exact form of the CM angular and energy distributions, they do place certain constraints on the fits. The best fits were obtained with $T(\theta)$ distributions that peak at 0° and 180° with maxima at 0° (fig. 5). There is a range of

acceptable values for the $P(E')$ parameters (as there is for the coefficients of the Legendre polynomials that constitute $T(\theta)$) yet the average energy, $\langle E' \rangle$ (table 1), does not vary much within this range. Since the fits were relatively insensitive to the q parameter, which governs the curvature of the tail of the $P(E')$, this parameter was fixed for all the fits and the other parameters optimized. The resulting $P(E')$'s (fig. 6) peak between 0.0 and 1.2 kcal/mol, with the *o*-BT $P(E')$'s peaking at lower energies and having slightly lower values of $\langle E' \rangle$ than those for *p*-BT. The following changes in the $P(E')$ for *p*-BT, $E_c=25.3$ kcal/mol, while not significantly affecting the fit, produced the indicated changes in $\langle E' \rangle$: $\pm 25\%$ in q , $\pm 10\%$ in $\langle E' \rangle$; ± 0.4 kcal/mol in peak position, $\pm 2\%$ in $\langle E' \rangle$; ± 2 kcal/mol in endoergicity, $\pm \sim 15\%$ in $\langle E' \rangle$. A CM frame product flux contour diagram for $\text{Br} + \text{p-CT} \rightarrow \text{p-BT} + \text{Cl}$, $E_c=31.5$ kcal/mol, is given in fig. 7. The overall quality of the fits justifies our use of a separable form for the CM flux distribution.

The asymmetric CM angular distributions that we obtain indicate that the majority of 1-bromo,1-chloro,(2,4)methyl-cyclohexadienyl (BCMC) complexes decompose in a time less than one rotational period [8b]. The *p*-BT CM angular distributions show more forward-backward symmetry at lower collision energies, suggesting that the lifetime of the BC4MC complex increases relative to its rotational period as E_c decreases. We can estimate the rotational period of the BC4MC complex by assuming, for the sake of simplicity, that the Br atom collides perpendicular to the ring with an impact parameter of 0.9 \AA (the distance from the center of mass of *p*-CT to the chlorinated carbon) and that the rotational angular momentum of the reagent is negligible. For the collision of Br with *p*-CT, $E_c=31.5$

kcal/mol, the magnitude of the orbital angular momentum, \underline{L} , will be 160 \hbar . The moment of inertia about the rotation axis of the complex is ~ 840 amu \AA^2 , assuming that the halogenated carbon is sp^3 hybridized, that the C-Br and C-Cl bond lengths are 2.0 and 1.7 \AA respectively, and that the ring is undistorted. The rotational period, given by $\tau_{\text{rot}} = 2\pi I/L$, will therefore be 5 ps in the present example. At a collision energy of 21.4 kcal/mol, $\tau_{\text{rot}} = 6$ ps.

If we calculate the approximate product orbital angular momentum, \underline{L}' , for the p-CT reaction, $E_c = 31.5$ kcal/mol, using a relative velocity corresponding to $\langle E' \rangle_{\text{p-BT}} = 5.0$ kcal/mol and an impact parameter of 0.1 \AA (the distance between the chlorinated carbon and the center-of-mass of the complex, with the C-Cl bond perpendicular to the ring and the C-Br bond in the plane of the ring), we obtain $|\underline{L}'| = 15 \hbar$, far lower than the initial 160 \hbar . It would take an average exit impact parameter of ~ 1.1 \AA for the the total angular momentum of the complex to be carried away as product orbital angular momentum. However, even if most of the angular momentum of the collision were carried away in rotation of the BT product, the rotational energy of the product would be small (only ~ 1 kcal/mol for p-BT in the present example) because of its large moment of inertia ($I = 770$ amu \AA^2 for p-BT).

The lack of a strong correlation between \underline{L} and \underline{L}' is the reason why the CM angular distributions do not peak more strongly in the forward and backward directions [8a]. The larger amount of sideways scattering for o-BT at 31.0 kcal/mol could indicate an even weaker \underline{L} to \underline{L}' correlation in the Br

+ o-CT reaction at high collision energies. This may be due to the more complicated rotational motion of the asymmetric BC2MC complex.

A fraction of the translational energy of BT must come from rotation of the complex at its exit transition state (TS). In the absence of extensive vibration-rotation coupling in the complex, the rotational energy at this TS will be ~1.2 kcal/mol for BC4MC ($E_c=31.5$ kcal/mol, C-Cl bond perpendicular to the ring with a bond length of 2.6 Å [9]). If this energy went entirely into relative motion of the products, p-BT would acquire only 0.2 kcal/mol in translation. The rotational motion of BC2MC will, as noted above, be more complex. But the fact that the o-BT $P(E')$'s peak at slightly lower energies than those for p-BT could indicate that the ortho complex has a lower rotational energy at its exit TS than the para complex.

Lastly, relative cross sections, S_r , were calculated at the most probable collision energies by integrating the CM frame product flux:

$$S_r = 2\pi \int_0^{\infty} \int_0^{\pi} P(E') T(\theta) \sin\theta \, dE' d\theta .$$

The computed S_r were used to weight the collision energies used in the analysis. This procedure was repeated until the input and output values of S_r agreed. Final values of S_r as a function of E_c are given in table 1 and are plotted in fig 8.

A range of collision energies contributes to each value of S_r , although we assign each to a single, most probable collision energy. This spread in E_c is the dominant source of uncertainty in the the derivation of S_r . Another source, however, is the uncertainty in the form of the $P(E')$. By fixing the q parameter in the fits, we believe that we have eliminated this source of uncertainty in the relative cross sections.

DISCUSSION

The endoergicities of the different isomeric reactions under study should not differ markedly from one another. The heats of formation of o,m, and p-CT ($\Delta H_{f298}^{\circ}(\text{g})$) are 3.8, 4.1, and 5.3 kcal/mol respectively [10,11]. We were able to find heat of formation data for the para isomer of bromotoluene (BT) only ($\Delta H_{f298}^{\circ}(\text{g})=13.0$ kcal/mol [11,12]), but Szwarc's work [13] indicates that the C-Br bond dissociation energies (BDE) in o,m, and p-BT differ by only 0.6 kcal/mol. Using the known values for ΔH_{f298}° of Br, Cl [30], p-CT, and p-BT, we calculate $\Delta H_{298}^{\circ}=10.1$ kcal/mol for the reaction, $\text{Br} + \text{p-CT} \rightarrow \text{p-BT} + \text{Cl}$. This number strikes us as being too low considering that $\Delta H_{298}^{\circ}=15$ kcal/mol for the reaction, $\text{Br} + \text{C}_6\text{H}_5\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{Br} + \text{Cl}$ [15]. In the absence of firm values for the heats of formation of the CT and BT isomers, we have used an endoergicity of 15 kcal/mol for the present reactions.

The energetics of Br addition to CT are, as far as we can tell, unknown. Ref. 14 gives $\Delta H=-8.8$ kcal/mol for $\text{Br} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4\text{Br}$. The exothermicity of Br addition to benzene will be decreased by the loss in resonance stabilization energy (RSE) that results from the disruption of the π -electron framework of the ring. In the case of H atom addition to benzene the loss in RSE will be approximately 11 kcal/mol [16]. We conclude, therefore, that the BCMC radical will be unbound by ~ 2 kcal/mol relative to reactants! Benson et. al. [17] arrive at a similar value for the endothermicity of Br addition to benzotrifluoride. As a result, we do not expect there to be a potential minimum along the reaction coordinate corresponding to the BCMC complex.

Based on the energetics for Br addition to CT, it is not surprising then that substitution occurs in less than one rotational period. We have calculated RRKM lifetimes, τ_{RRKM} , for the BCMC complex [20], using modified normal mode frequencies for toluene, and frequencies corresponding to C-Cl and C-Br stretching and Br-C-Cl, C-C-Br, and C-C-Cl bending modes [21]. Including all 42 frequencies, τ_{RRKM} at $E_c=30$ kcal/mol ($E^*=28$ kcal/mol) is 0.02 ps, much lower than the estimated rotational period. τ_{RRKM} changes little as the collision energy is lowered, indicating that a quantitative comparison of the angular distribution data with the lifetime and rotational period calculations is not possible. It is interesting to note, however, that product angular distributions measured for the reaction $\text{Br} + \text{CH}_2\text{CCl}_2 \rightarrow \text{Cl} + \text{CH}_2\text{CBrCl}$ [18] are symmetric about the center-of-mass angle. In this reaction, adduct formation is indeed exoergic.

Remarkably, very little of the energy available to the products ends up in translation. Apparently the vibrational modes of the aromatic ring act as a strong energy sink with Cl elimination occurring only when sufficient energy has accumulated in the C-Cl bond. Yet, although intramolecular vibrational energy redistribution appears to be extensive prior to C-Cl bond rupture (there is certainly much in the current literature that indicates that, at these energies, it should be [19]), it does not seem likely that Cl elimination from BCMC is a statistical process involving energy sharing among a large number of vibrational degrees of freedom. We have calculated RRKM-AM $P(E')$'s [22] for BT, $E_c=31$ kcal/mol, using different numbers of vibrational modes and a variety of values for the maximum centrifugal barrier, B_m . Since the activation energies for Cl addition reactions are

known to be very near zero [23], we have no reason to expect that there will be a barrier above the threshold for Cl elimination. Although a definitive comparison between the experimental and RRKM $P(E')$'s is not possible given the uncertainties in the fits, we obtain reasonable agreement between the experimental *o*-BT $P(E')$, $E_c=31.0$ kcal/mol, and a 4-mode ($\nu=800-700$ cm^{-1}) RRKM $P(E')$ with a B_m value of 0.028 (fig. 6). Using 6 modes ($\nu=900-700$ cm^{-1}) gave a $P(E')$ that fell too steeply. Thus, the data seem to indicate that only a limited number of degrees of freedom in the vicinity of the collision participate in energy sharing prior to Cl elimination.

Such a mechanism is not unexpected. Endoergic substitution at high collision energies must occur in a quasi-direct fashion or not occur at all since, as more vibrational modes participate in energy redistribution, the probability of Cl elimination, η_{Cl} , drops relative to η_{Br} . This is due to the fact that η_X is proportional to the density of states at the TS for X elimination. The smaller the number of active vibrational modes, the smaller the difference between the state densities for the exoergic and endoergic channels and the more Cl elimination will compete with Br elimination. For example, taking η_X to be the microcanonical RRKM rate constant for X elimination, at $E_c=30$ kcal/mol $\eta_{Br}/\eta_{Cl}=270$ with 12 active modes ($\nu=800-300$ cm^{-1}) whereas with 6 active modes $\eta_{Br}/\eta_{Cl}=15$.

We attempted to determine the relative importance of the Br elimination channel in both the *p*-CT reaction, $E_c=21.4$ kcal/mol, and the *o*-CT reaction, $E_c=31.0$ kcal/mol, by measuring the TOF of CT from the channel $\text{BCMC} \rightarrow \text{Br} + \text{CT}$ near the center-of-mass angle. In both cases, the TOF of non-reactively scattered CT obtained by substituting Kr for Br was very

similar to that obtained with Br. This indicates that the Br addition cross section is substantially smaller than the elastic/inelastic scattering cross section. Yet, if η_{Br} were indeed two orders of magnitude larger than η_{Cl} (as one would predict from a 12-mode RRKM calculation), we would have been able to see a substantial peak in the o-CT TOF spectrum corresponding to slow o-CT travelling at the velocity of the center-of-mass since the fast and slow components of the elastic scattering TOF spectrum were well resolved at $E_c=31.0$ kcal/mol. Thus, our inability to observe slow o-CT provides additional (though indirect) evidence that only a few modes are active during the reaction.

Further support for the reduced mode mechanism comes from an examination of the excitation functions. The measured relative cross sections can be expressed as the product of the cross section for forming the BCME adduct and the relative probability of decomposition of the adduct through Cl elimination, $S_r = \sigma_{add}[\eta_{Cl}/(\eta_{Cl} + \eta_{Br})]$. If σ_{add} were constant over the energy range studied, and intramolecular energy randomization were complete prior to atomic elimination, the quantity in brackets would be equivalent to the RRKM branching ratio, S_{RRKM} . We have calculated S_{RRKM} for the present system, using 35 ($\nu=1600-200$ cm^{-1}), 12, 6, and 3 ($\nu=800-700$ cm^{-1}) modes. The 35- and 12- mode curves both rise steeply with energy and are essentially identical in slope. The 3- and 6-mode curves, scaled to $S_{r,p-BT}$ and $S_{r,o-BT}$ respectively, are plotted in fig 8 alongside the experimental results. There is good qualitative agreement between the slopes of $S_{RRKM}(6\text{-mode})$ and $S_{r,o-BT}$, and between the slopes of $S_{RRKM}(3\text{-mode})$ and $S_{r,p-BT}$.

It is certainly plausible that the BC2MC collision complex has a larger number of active vibrational modes than BC4MC. We have already noted that the o-BT $P(E')$'s have slightly lower values of $\langle E' \rangle$ than those for p-BT. The reduced symmetry of the BC2MC complex may allow for enhanced vibrational energy redistribution through state mixing. Coupling of the internal rotation of the methyl group to the ring vibrations is believed to be responsible for accelerated IVR in S_1 p-fluorotoluene [19c,24]. Although the barrier to methyl torsion is likely to be higher in o-CT than in p-CT [25], the methyl group is closer to the collision site in the ortho isomer.

The normalization factor used to scale $S_{RRKM(6\text{-mode})}$ to $S_{r,o\text{-BT}}$ is a factor of 5 higher than that used to scale $S_{RRKM(3\text{-mode})}$ to $S_{r,p\text{-BT}}$ indicating, in the present context, that σ_{add} for Br + o-CT is 5 times higher than for Br + p-CT. A higher addition cross section for o-CT can be rationalized along the above lines. The greater number of active modes in BC2MC might serve to dissipate the energy of the collision better, allowing Br to add more readily to o-CT than to p-CT.

There still remains the possibility that σ_{add} changes with energy. If this were true, one could not attribute the energy dependence of S_r solely to the statistical branching ratio. Using a semi-empirical potential energy surface (PES) to calculate classical trajectories, Hase et. al. [26] found that the cross section for H atom addition to C_2H_4 varies with collision energy and that this variation is dependent on the shape of the entrance valley of the PES. Perhaps, then, the lower cross section that we observe for o-CT substitution below $E_c=25$ kcal/mol reflects a narrowing of the acceptance angle of the PES as a result of the presence of the methyl

group. If this were the case, the methyl group would also raise the effective threshold for Cl elimination. One might imagine, therefore, that the o-BT excitation function could be modeled using a higher endoergic threshold and a smaller number of modes. We investigated this by calculating S_{RRKM} using 3 modes and $E_0=17-20$ kcal/mol. Although the closest agreement with $S_{r,o-BT}$ was obtained with $E_0=18$ kcal/mol, the calculated branching ratio fell much more rapidly to zero than the experimental excitation function. If a reduced cross section for Br addition at lower energies were included, the calculated excitation function would disagree even more sharply with the experimental result.

Based on our experimental signal levels, the substitution cross section for m-CT must be at least a factor of 10 lower than for o-CT at $E_c=31.0$ kcal/mol. It is well known that the methyl group is an ortho-para directing substituent in electrophilic (ionic and atomic) substitution reactions. This phenomenon is usually explained in terms of the electron donating capability of the methyl group, which stabilizes the o- and p- adducts by either increasing the o- and p- frontier electron populations in the reactant molecule or lowering the total π -electron energy of the o- and p- adducts relative to the m- adduct [27]. Considering the large excess of translational energy at $E_c=31.0$ kcal/mol, however, it is difficult to understand how the decreased stability of the BC3MC complex could cause the m-CT cross section to be so low.

A possible explanation is that the reactivities of the isomers of CT are governed by the shape of the Br-CT PES rather than by fixed barriers. The increased electron populations ortho and para to the methyl group in CT

could enhance the long range attraction between Br and these sites, but again, this effect is unlikely to be strong at high collision energies. The shape of the potential in the exit valley might be the key [28]. By microscopic reversibility, the reverse reactions, $\text{Cl} + o-,p\text{-BT} \rightarrow \text{Br} + o-,p\text{-CT}$, must also be accelerated. A longer range attraction between Cl and $o-$ and $p\text{-BT}$ will manifest itself in a more gradually sloping potential in the reverse endoergic direction. Alternatively, the lower π -electron energies of the BC(2,4)MC complexes could cause the $o-$ and $p-$ surfaces to rise more gradually. In either case, translational energy will be better able to promote the endoergic reaction. Classical trajectory studies on several different potential energy surfaces lend support to these ideas. Polanyi et. al. [28b] have observed that translational energy is favored over vibrational energy in endoergic reactions with a gradual ascent to the barrier crest. Likewise, Chapman [29] has found that the curvatures of the $\text{Be} + \text{HF} \rightarrow \text{BeF} + \text{H}$ and $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ surfaces have marked effects on the excitation functions and product energy distributions of these reactions.

In conclusion, both limited intramolecular vibrational energy redistribution and the slope of the potential energy surface along the reaction coordinate are likely to be responsible for the interesting dynamics that we observe for these substitution reactions.

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Table 1: Relevant experimental quantities.

Reaction	$E_c^{(a)}$	$\langle E' \rangle$	S_r (arb. units)	$n_{Br} n_{CT} v_{rel}$
Br/He + p-CT	31.5	5.0	0.71	0.98
Br/Ne + p-CT	25.3	3.1	0.48	0.59
Br/Ar + p-CT	21.4	2.1	0.31	0.53
Br/He + o-CT	31.0	4.6	1.00	1.00
Br/Ne + o-CT	25.3	2.9	0.45	0.54
Br/Ar + o-CT	20.9	1.9	0.18	0.44
Br/He + m-CT	~31.0	---	0.00	*

(a): All energies are in kcal/mol

*: The m-CT reaction was studied several weeks after the o- and p-CT experiments were completed. The Br/He + o-CT angular distribution was re-measured at this time, however. The o-BT and Br elastic signal levels indicated that the Br beam intensity was ~50% lower than during the earlier experiments; the o-BT signal-to-noise ratio had dropped by 20%. However, given the presence of elastic scattering background in the m-CT experiment (~2 Hz at 460), it is doubtful that we would have been able to see signal even if the Br beam were twice as intense.

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Figure captions:

Figure 1: Generalized reaction coordinate diagram. Shaded region indicates approximate collision energy range.

Figure 2: o- and p-BT laboratory angular distributions (m/e 170) normalized to constant reactant flux. Br beam is at 0° . Solid lines are fits to data. Arrows indicate positions of center-of-mass angles with collision energy decreasing from left to right.

o-BT: ○ : $E_C=31.0$ kcal/mol, ▲ : $E_C=25.3$, □ : $E_C=20.9$

p-BT: ○ : $E_C=31.5$ kcal/mol, ▲ : $E_C=25.3$, □ : $E_C=21.4$

Figure 3: Time-of-flight spectra of p-BT, $E_C=31.5$ kcal/mol (m/e 170), at five different angles. Solid lines are fits to data.

Figure 4: (a) TOF spectra of o-BT, $E_C=25.3$ kcal/mol.
(b) TOF spectra of p-BT, $E_C=21.4$ kcal/mol.
(c) TOF spectrum of o-BT, $E_C=20.9$ kcal/mol.
Solid lines are fits to data.

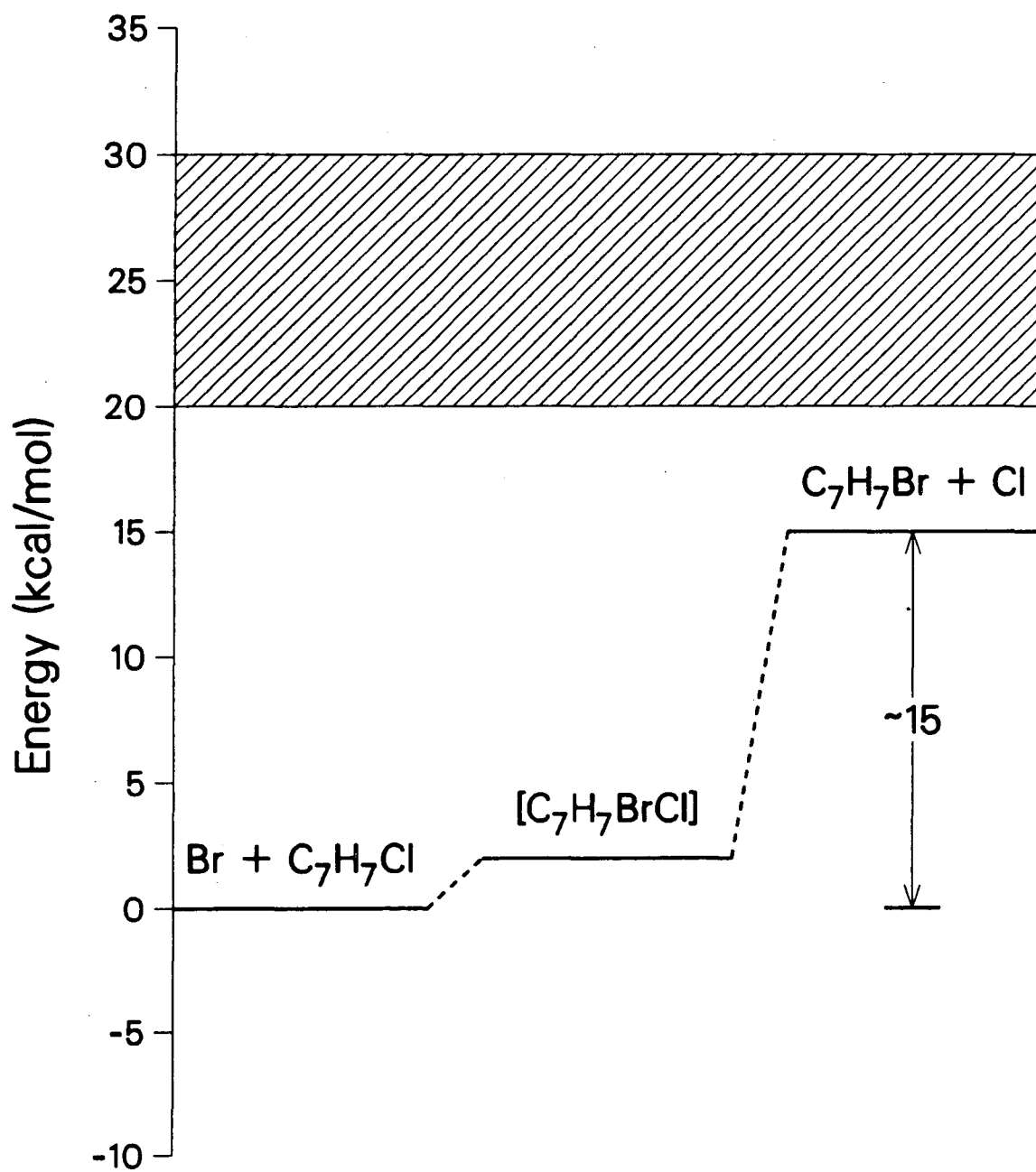
Figure 5: CM frame product angular distributions:
—— : o-BT: $E_C=31.0$ kcal/mol, p-BT: $E_C=31.5$
- - - : o- and p-BT: $E_C=25.3$.
- • - : o-BT: $E_C=20.9$, p-BT: $E_C=21.4$

Figure 6: CM frame product translational energy distributions:
—— : o-BT: $E_C=31.0$ kcal/mol, p-BT: $E_C=31.5$
- - - : o- and p-BT: $E_C=25.3$.
- • - : o-BT: $E_C=20.9$, p-BT: $E_C=21.4$
•••• : 4-mode RRKM translational energy distribution

Figure 7: CM frame product flux contour diagram for p-BT, $E_c=31.5$ kcal/mol
Scale given is for contour diagram. Scale of Newton diagram is
half that of contours. Center-of-mass velocity vector is
represented by arrow between beam vectors.

Figure 8: Plot of relative cross section vs collision energy.

● : p-BT; ■ : o-BT; □ : m-BT
—— : 3-mode RRKM branching ratio curve. Normalized to equal
 $(0.99)S_{r,p-BT}$ at 31.5 kcal/mol.
- - - : 6-mode RRKM branching ratio curve. Normalized to equal
 $(0.97)S_{r,o-BT}$ at 31.0 kcal/mol.



XBL 876-2875

Fig. 1

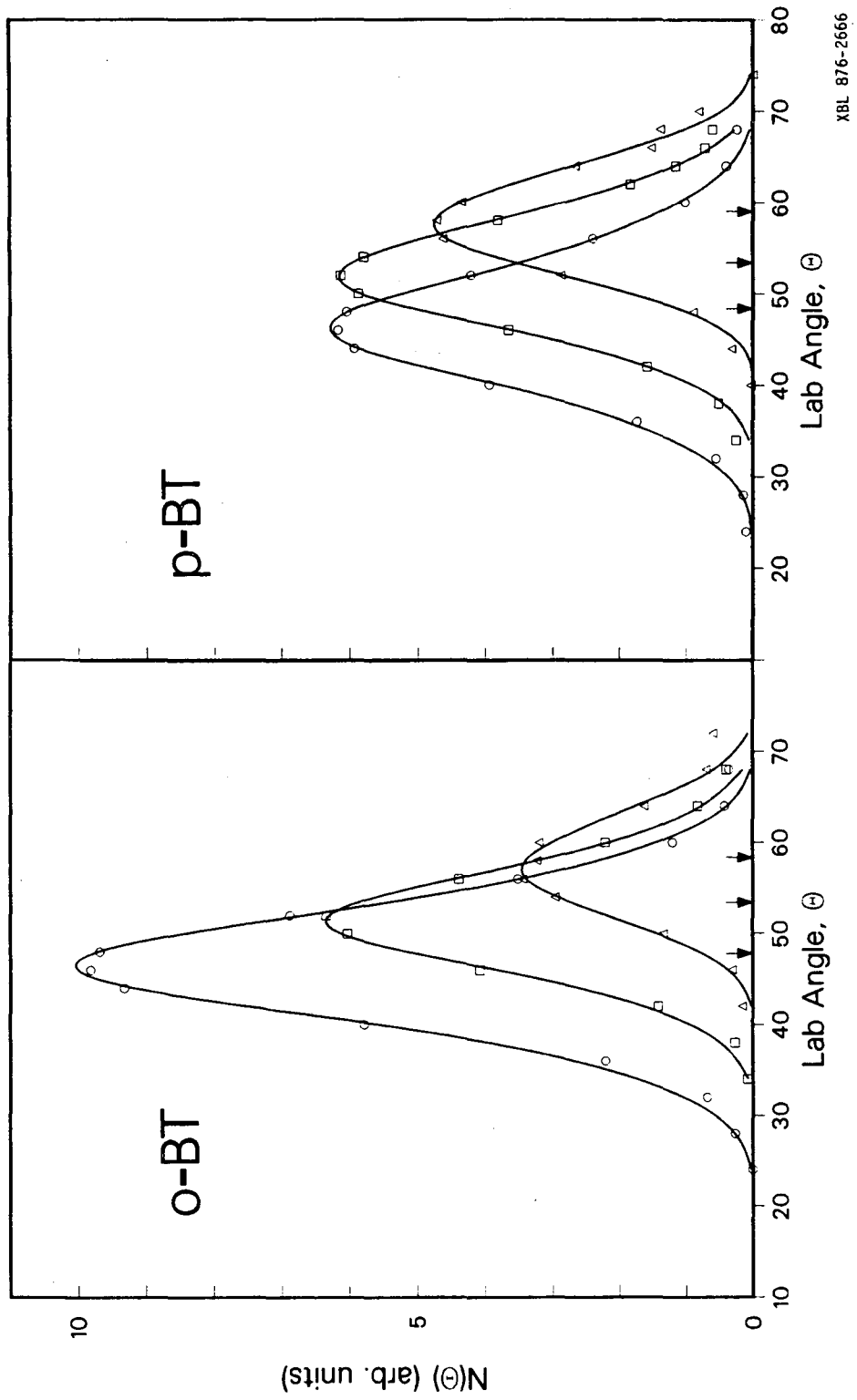
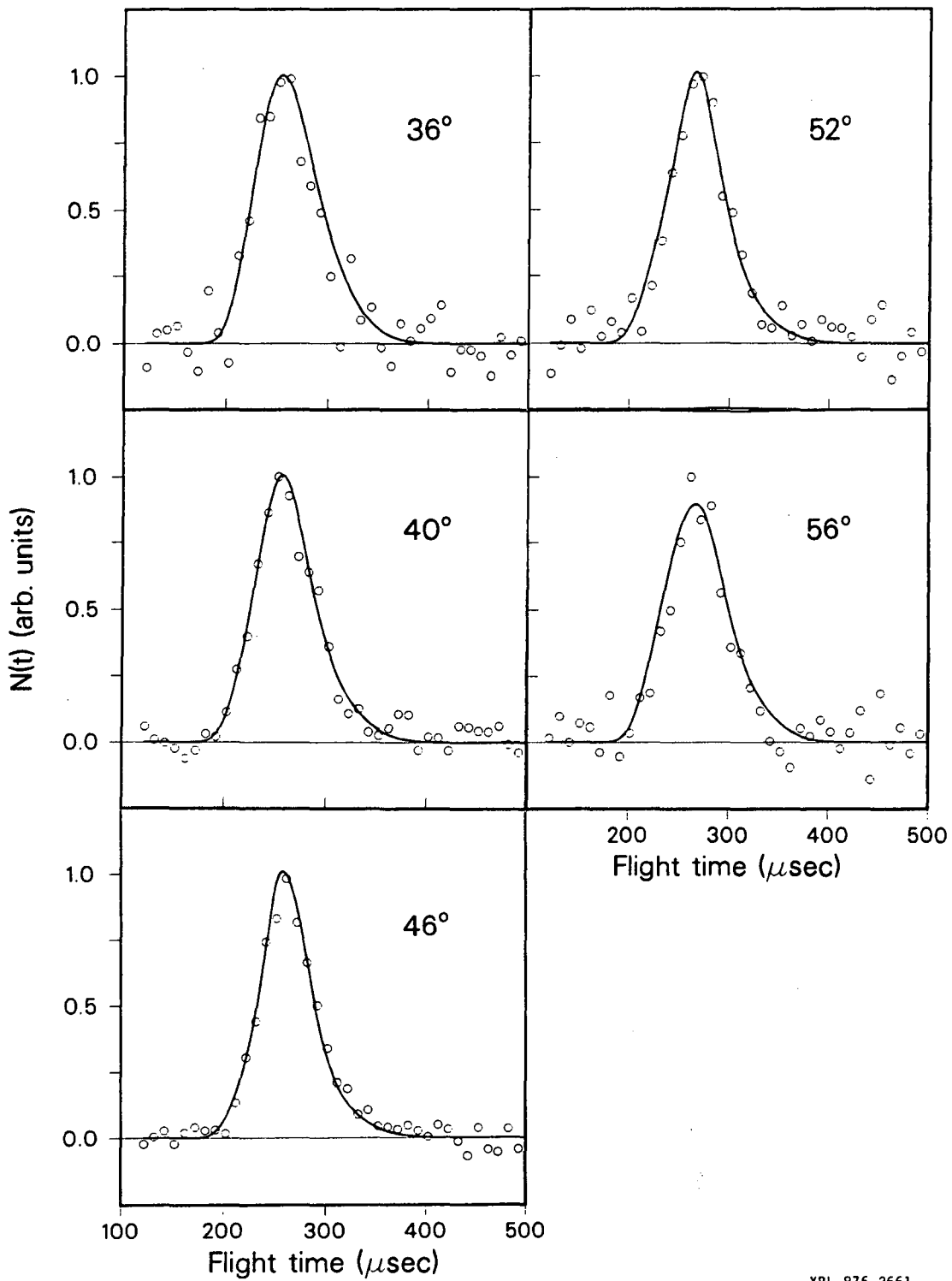
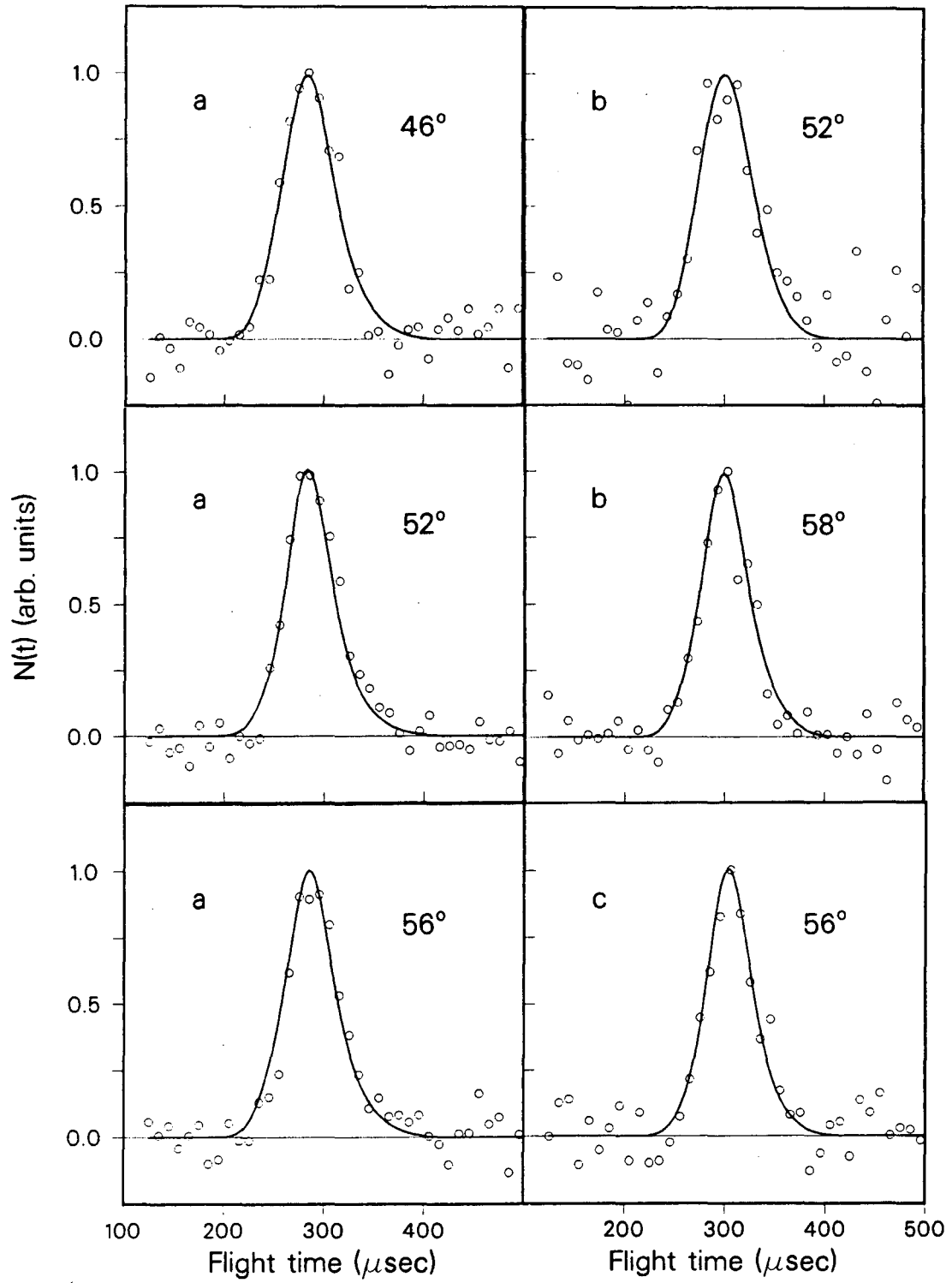


Fig. 2



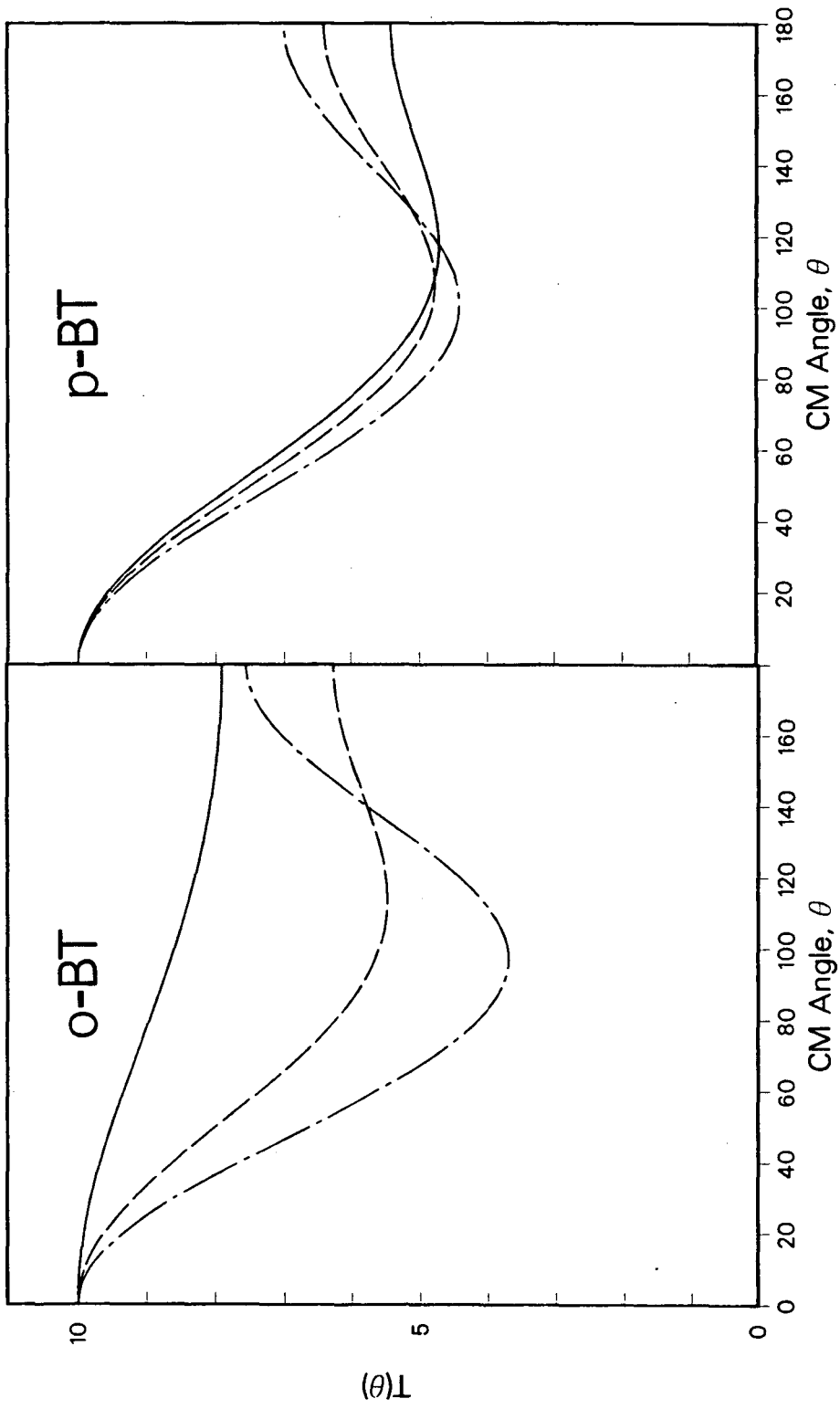
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Fig. 3



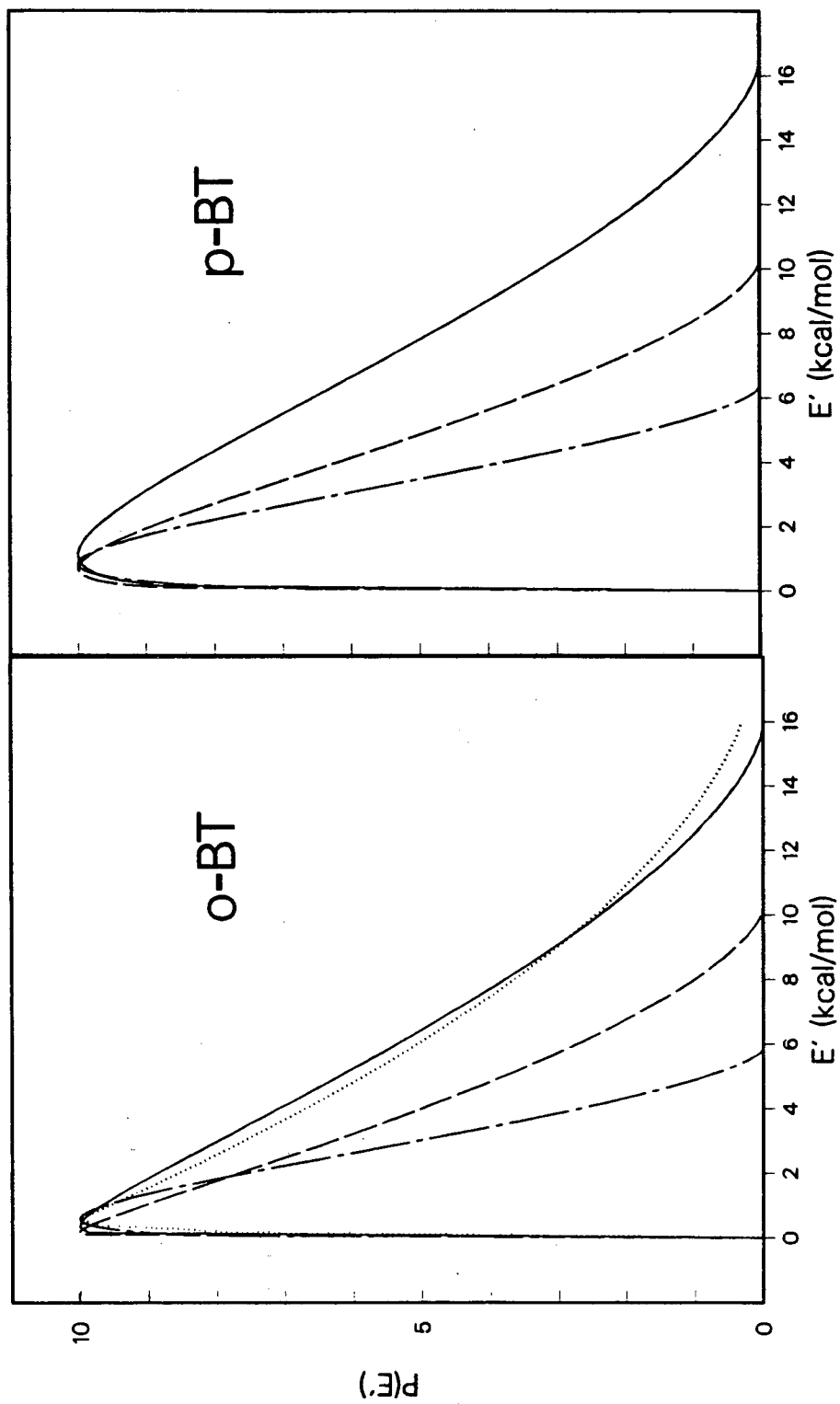
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Fig. 4



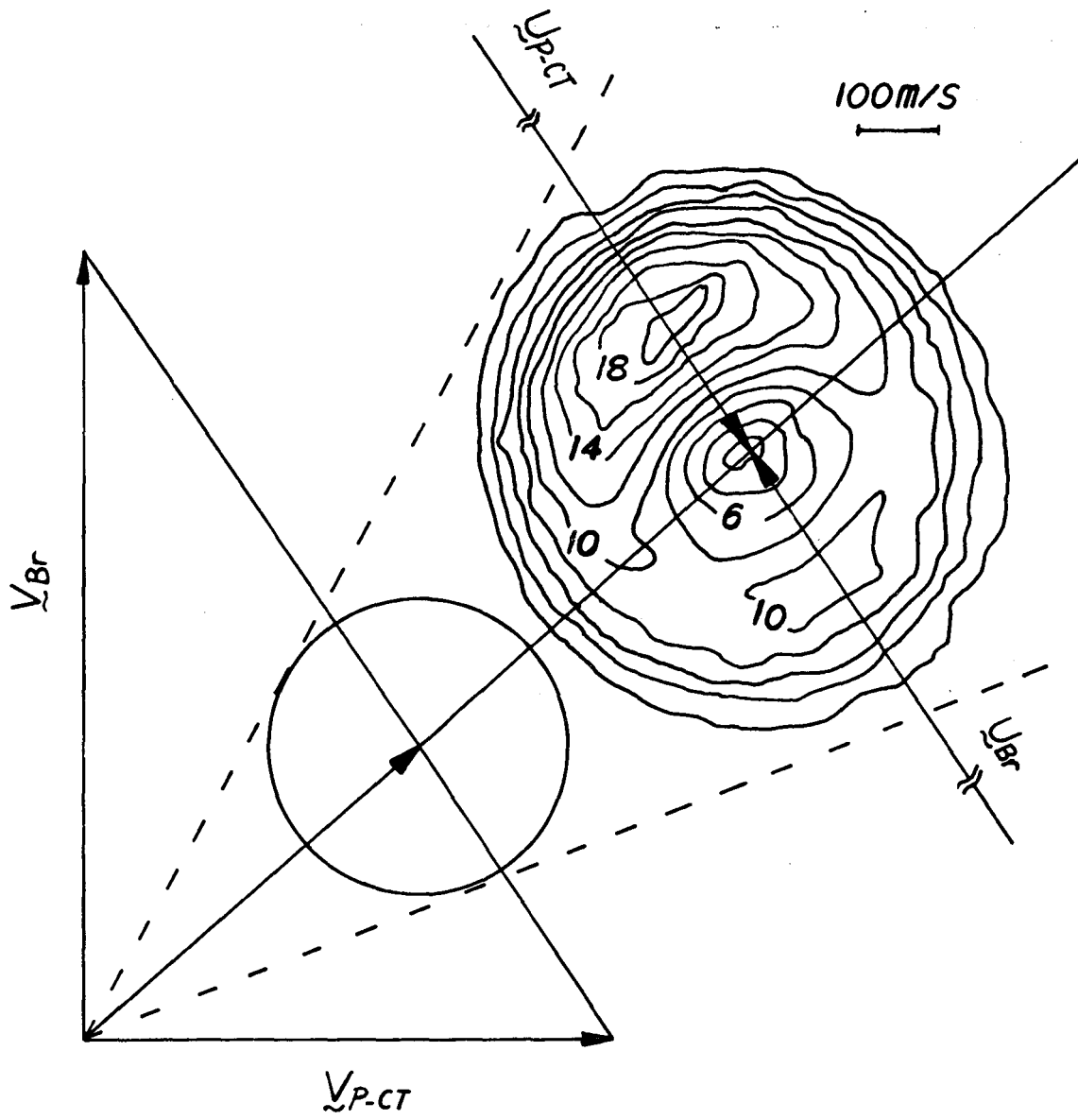
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Fig. 5



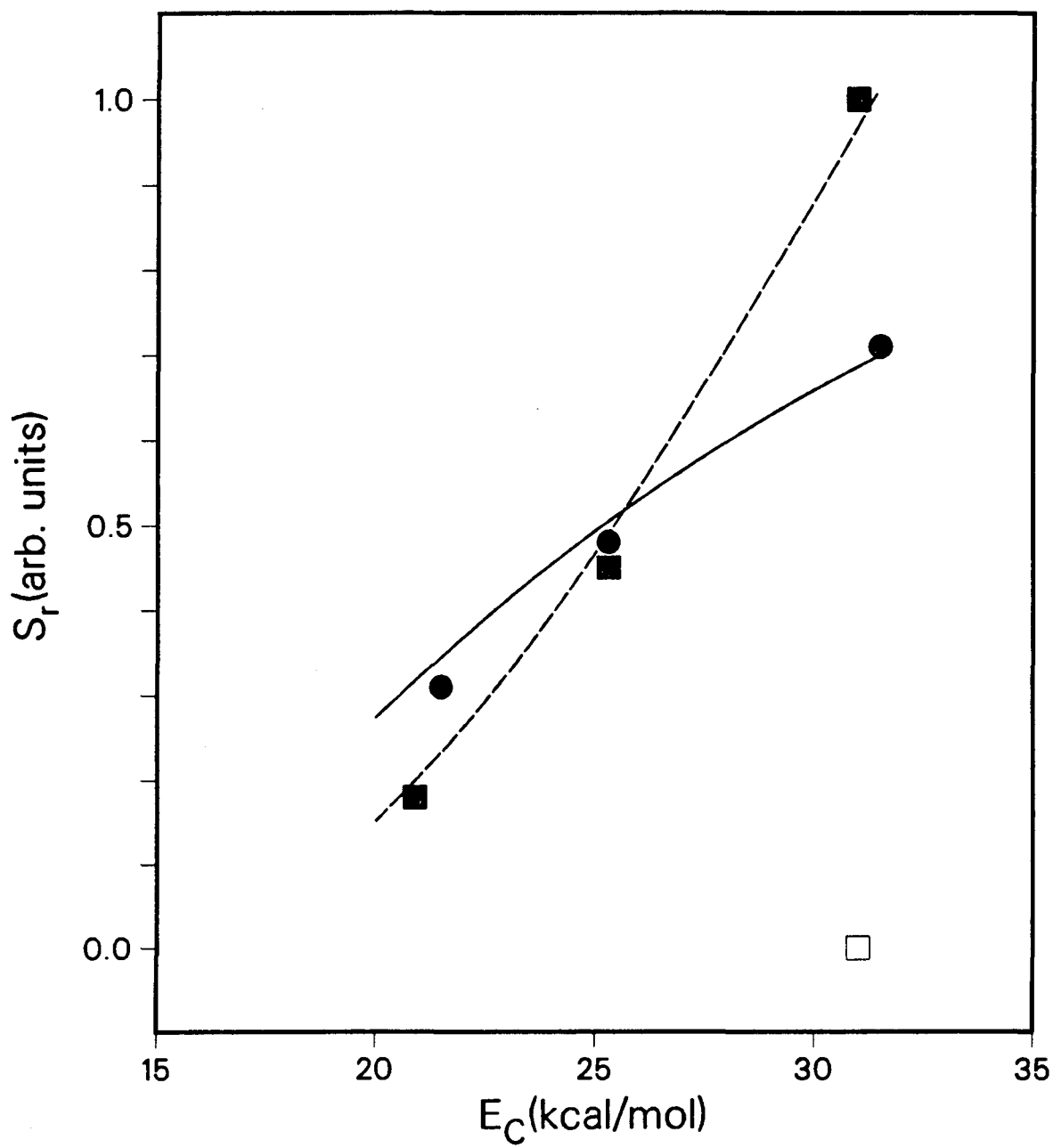
XBL 876-2665

Fig. 6



XBL 876-2662

Fig. 7



XBL 876-2876

Fig. 8

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