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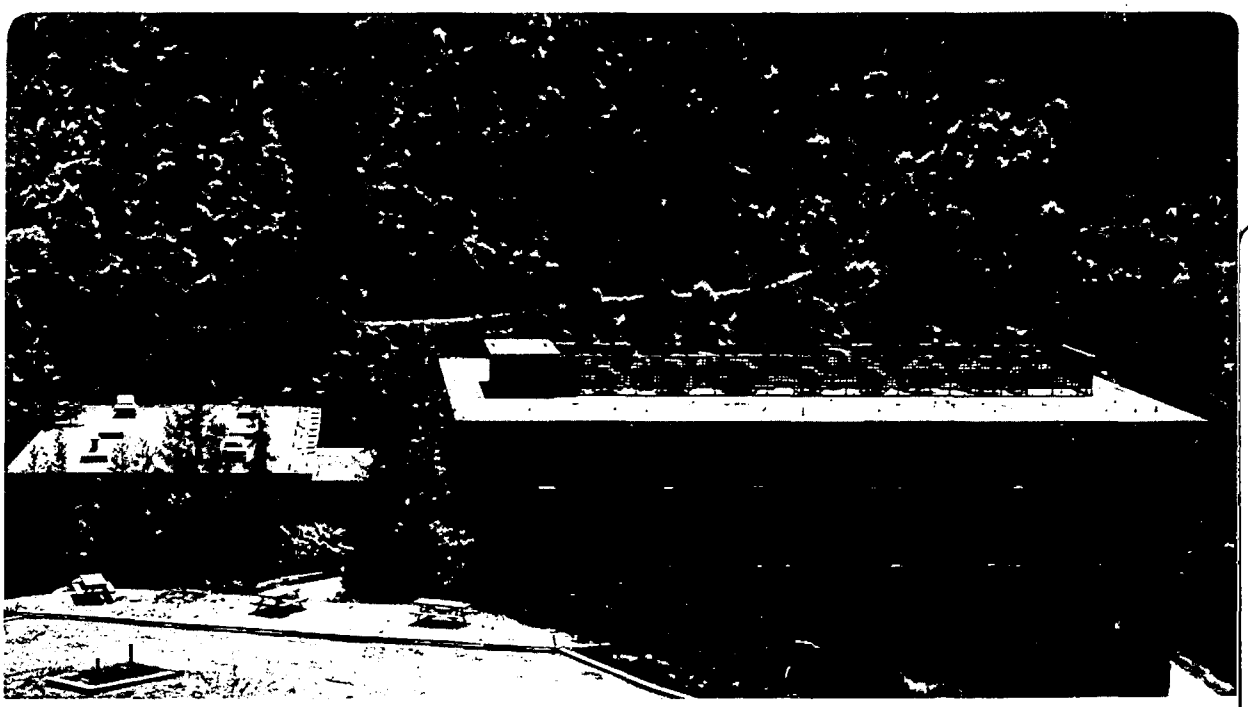

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CROSSED MOLECULAR BEAM STUDY OF THE REACTION $O(^3P) + C_2H_4$

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ABSTRACT

The reaction between ground state atomic oxygen and ethylene was studied under single collision conditions using the crossed molecular beam method. At an average collision energy of about 6 kcal/mole, the two major primary reaction channels are (a) the formation of CH_3 and CHO and (b) the formation of C_2H_3O and H. Product angular distributions and time-of-flight spectra were measured and the translational energy release was determined for each channel. The observed results and calculated potential energy surfaces suggest that after the addition of $O(^3P)$ to ethylene forming a triplet diradical, channel (a) occurs by way of intersystem crossing to the singlet state, 1,2-H migration and subsequent C-C bond rupture, whereas channel (b) proceeds mostly through the direct dissociation of the intermediate triplet diradical, except for a small contribution from H atom elimination of the singlet acetaldehyde intermediate.

Introduction

The reaction of $O(^3P)$ with ethylene plays an important role not only in the combustion of ethylene itself, but also for many other fuels since ethylene is an important intermediate in the combustion of methane,[1,2] larger aliphatic hydrocarbons,[3] and aromatics.[4] In ethylene flames, the fuel consumption by oxygen atoms plays a crucial role[2,5-7] although the reaction of ethylene with OH radicals appears to dominate, particularly at higher temperatures.[6,7]

Westbrook[7] has developed a comprehensive mechanism for ethylene combustion which has been extended and successfully applied to many kinds of experimental conditions.[6,8] For modeling combustion systems, detailed knowledge of all the primary chemical processes involved, their rate coefficients, and the identity of all reaction channels are necessary.

Good agreement has been obtained for the rate coefficient of the overall reaction of $O(^3P)$ with C_2H_4 over a wide range of temperatures.[9] The Arrhenius plots are definitely curved and good fits are obtained by using double-exponential expressions.

The identity of the primary reaction products and their relative importance has been a subject of considerable controversy for many years. However, a clear picture seems to be emerging from various recent experimental investigations. We present here the results of a new molecular beam investigation which provides an answer to the question of the major primary reaction channels and

the reason for some of the apparent contradictions.

Previous work on the $O(^3P) + C_2H_4$ reaction was reviewed recently by Cvetanovic and Singleton.[10] The following reactions have been considered as possible primary channels:

$$O(^3P) + C_2H_4 \rightarrow CH_3 + CHO \quad (1a)$$

$$O(^3P) + C_2H_4 \rightarrow H + CH_2CHO \quad (1b)$$

$$O(^3P) + C_2H_4 \rightarrow H_2 + CH_2CO \quad (1c)$$

$$O(^3P) + C_2H_4 \rightarrow CH_2 + CH_2O \quad (1d)$$

$$O(^3P) + C_2H_4 \rightarrow C_2H_4O \quad (1e)$$

$$O(^3P) + C_2H_4 \rightarrow OH + C_2H_3 \quad (1f)$$

Cvetanovic[11,12] suggested a mechanism of electrophilic addition of the oxygen atom in the ^3P state to one of the olefinic carbon atoms, followed by rearrangement or fragmentation of the initially formed triplet diradical $(CH_2CH_2O)^{\ddagger}$. Intersystem crossing (ISC) to the ground state singlet surface and stabilization of the adduct through collisions, channel (1e), was indeed observed in cold rare gas matrices[13,14] and in the gas phase at high pressure.[15,16] Eusuf and Wagner[15] found only acetaldehyde at pressures of 20-80 atm., whereas Bley et al.[16] detected both acetaldehyde and ethylene oxide at pressures of 4-70 atm. Vinyl alcohol was only found in the matrix study by Hawkins and Andrews,[14] but was possibly due to the reaction of $O(^1D)$ in that experiment.

In the absence of stabilizing collisions, the intermediate

diradical or its rearrangement products undergo fragmentation. Although some early work[17] suggested channel (1d), the formation of formaldehyde and methylene, to be the major primary route, most authors[11,18-21] found channel (1a), formation of methyl radical and formyl radical, to be dominant. From the stoichiometric balance, Cvetanovic[18] suggested the existence of additional channels: the formation of hydrogen atom and the vinoxy radical C_2H_3O, channel (1b), and the formation of molecular hydrogen and ketene, channel (1c), although ketene was not detected as a product in their experiment. The high-intensity molecular beam experiments with mass spectrometric detection carried out later by Gutman and coworkers[20] and Blumenberg et al.[21] did identify (1c) as a minor channel, accounting for about 5% of the products.

Channel (1f), abstraction of H to form OH and vinyl radical, is endothermic by approx. 6 kcal/mole[22] and is assumed to proceed without an intermediate collision complex, but with a barrier of about 12 kcal/mole.[23] It was never observed directly but is assumed to play an important role at higher temperatures[7] and may explain the origin of the curvature in the $O(^3P) + C_2H_4$ Arrhenius plots.

While it appeared that agreement had been reached that channel (1a), formation of CH_3 and CHO, was the dominant process in the $O(^3P) + C_2H_4$ reaction, more recent experimental and theoretical results led to a different conclusion. A molecular beams experiment conducted in our laboratory[24] firmly established channel (1b), formation of H atoms and C_2H_3O, as an important primary

process from the measurements of product angular distributions. In another crossed molecular beam experiment, Clemo et al.[25,26] also detected the vinoxy radical and obtained a threshold value of 1.2±0.7 kcal/mole for this process.

Spectroscopic information about the vinoxy radical became available from an LIF experiment by Inoue and Akimoto[27] and UV absorption[28] and was used by Kleinermanns and Luntz[29] and Hunziker et al.[28] to identify vinoxy as a product in the $O(^3P) + C_2H_4$ reaction.

Ab initio calculations for the structure and energetics of vinoxy were performed[30,31] and it was determined[31,32] that of the two possible resonance structures, formylmethyl (with the unpaired electron centered on the carbon atom) actually dominates.

Channel (1a), formation of CH_3 + CHO, was not observed in the earlier crossed molecular beam experiment,[33] which was attributed to the fact that this channel requires an unlikely 1,2-hydrogen migration in the triplet diradical adduct. The barrier for this process would be higher than the internal energy of the complex.[34] ISC was thought to be slow because the spin-orbit-interaction is supposed to be weak in a molecule that small.[24] However, CHO was observed using UV absorption by Hunziker et al.[28] and using laser magnetic resonance (LMR) by Temps and Wagner[35] in the same system. Hunziker et al.[28] suggested a mechanism whereby ISC in the diradical could be induced by collisions, followed by facile 1,2-hydrogen migration on the singlet surface and subsequent C-C-bond rupture. The CHO yields of Temps and Wagner[35] indeed showed a

decrease with decreasing pressure in the range of approx. 1-4 Torr.

In order to resolve the question of the pressure dependence of the reaction mechanism and branching ratios, experiments were conducted over a large pressure range by many research groups as summarized in Table I. These results suggest that the branching ratio between channel (1a) and (1b) is relatively insensitive to the pressure over a large pressure range (30 mTorr - 760 Torr), and that these channels are about equally important. Although in all cases secondary reactions had to be taken into account, the low pressure experiments appeared to present mounting evidence that channel (1a) is not a result of collision-induced intersystem crossing. The question whether intersystem crossing in diradical intermediates can effectively compete with channel (1b) under collision free conditions, can be answered definitively by an improved crossed molecular beam experiment.

The problems arising with this particular reaction in a crossed beam experiment are twofold: First, due to the unfavorable kinematics, as discussed below, products from channel (1a) are expected to be much harder to detect than those from channel (1b). Second, for mass spectrometric detection, the coincidence of the expected ionic signal from products of channel (1a) at m/e=15, 28, and 29 with major background peaks presents difficulties. By using $^{18}O_2$ and an improved experimental arrangement, we have overcome these problems and reinvestigated the $O(^3P) + C_2H_4$ reaction as well as the $O(^3P) + C_2H_2$ reaction.[39]

Experimental

The experimental setup has been described in detail recently.[39] Briefly, continuous supersonic molecular beams of oxygen atoms and ethylene were crossed at an angle of 90° in a vacuum chamber. Scattered species were detected using a triply differentially pumped detector equipped with an electron-impact ionizer, quadrupole mass filter, and Daly ion detector. The entire mass spectrometric detector was rotatable in the collision chamber around the intersection point of the two molecular beams.

The high pressure supersonic oxygen atom beam source employed in these experiments was described in detail by Sibener et al.[40] 400 to 600 Torr of 5% O_2 in Ne were expanded through 0.10-0.25 mm diameter quartz nozzles. The dissociation of O_2 was induced by a radio frequency discharge, and oxygen atoms in their ground (^3P) state were generated. The supersonic ethylene beam was formed by expanding pure ethylene gas at a backing pressure of 200 Torr through a nozzle of 0.15 mm diameter which was held at room temperature.

The peak velocities of the oxygen atom beam were between 1.8 and 2.1×10^5 cm/s with speed ratios around 5 and the peak velocity of the ethylene beam was 8.6×10^4 cm/s with a speed ratio of about 6, resulting in most probable collision energies of approximately 6 kcal/mole.

The measurement of the reaction products was carried out in

two different ways: First, the laboratory angular distributions of products at several ion masses were measured while modulating one of the beams for background subtraction. Typically, 6-8 angular scans were obtained for each m/e value, with total counting times of 6-16 min per angle. Second, TOF distributions were recorded at several laboratory angles and for several masses using the cross-correlation method.[41] Total accumulation times for the TOF-measurements ranged from a few minutes to several hours depending on the signal intensity of the particular ion.

For the TOF measurements in the present experiment, an important improvement to the standard arrangement[42] was achieved by reducing the number of differential pumping regions and increasing the angular spread of the hydrocarbon beam from three to two, enabling us to move the source closer to the interaction region, which resulted in an increase of approximately a factor of fifty in signal intensity.

The ethylene was obtained from Matheson with a stated purity of 99.99% min. and oxygen/neon mixtures were purchased from Matheson and Airco and had a stated minimum purity of 99.99% and 99.995%, respectively. $^{18}O_2$ with a stated isotopic purity of 95% minimum was kindly provided by Los Alamos National Laboratory and was mixed with neon of 99.995% stated minimum purity purchased from Airco. All gases were used without further purification.

Results and Analysis

Even though the parent ions produced from the products in the mass spectrometer detector fragment extensively and the interference from large amounts of nonreactively (elastically and inelastically) scattered reactants must be accounted for, positive identification of the primary reaction products is possible by identifying common features in different spectra for establishing parent-daughter ion relationships, and from the requirement that the total mass and the linear momentum of the reaction products need to be conserved.

Cross-correlation TOF was obtained at several different angles at the m/e ratios of 12, 13, 14, 15, 16, 24, 25, 26, 27, 28, 29, 30, 31, 32, 40, 41, 42, and 43 using ^{16}O, corresponding to the ions C^+, CH^+, CH_2^+, CH_3^+, O^+, C_2^+, C_2H^+, $C_2H_2^+$, $C_2H_3^+$, CO^+ or $C_2H_4^+$, CHO^+ or $^{13}C^{12}CH_4^+$, CH_2O^+, CH_3O^+, O_2^+, C_2O^+, C_2HO^+, $C_2H_2O^+$, and $C_2H_3O^+$ or $^{13}C^{12}CH_2O^+$ respectively; and at the m/e ratios 18, 27, 30, 31, 43 and 44 using ^{18}O, corresponding to the ions $^{18}O^+$, $C_2H_3^+$, $C^{18}O^+$, $CH^{18}O^+$, $C_2H^{18}O^+$, and $C_2H_2{}^{18}O^+$, respectively. Angular distributions were measured at m/e ratios of 12, 13, 14, 15, 16, 27, 28, 29, 30, 32, 41, and 42 using ^{16}O only. No measurements could be taken at m/e=1 and 2 in the present experiment.

A forward-convolution method was used for the analysis in order to find the product translational energy distribution, $P(E_T)$, and the angular distribution, $T(\theta)$, in the center-of-mass (CM) frame. $P(E_T)$ and $T(\theta)$ were assumed to be independent of each

other. Furthermore, the relative cross-sections were assumed to be independent of the collision energy within the range of collision energies in this experiment. From the $P(E_T)$ and $T(\theta)$ functions, laboratory angular distributions and TOF spectra were calculated and averaged over beam velocities, collision angles, the detector acceptance angle and the length of the ionizer in the mass spectrometer and then scaled to the experimental data. The distributions were altered and the calculations repeated until a best fit to the experimental data was found. For maximum flexibility, the $P(E_T)$ trial functions were not confined to a particular functional form. The $T(\theta)$ functions on the other hand were represented as linear combinations of Legendre polynomials.

Major fragments of the vinoxy radical, the product of channel (1b), are expected at m/e=14, 15, 24, 25, 26, 28, 29, 40, 41, 42, and 43 using ^{16}O. The products of channel (1a), CHO and CH_3, are expected to yield major fragments of m/e=29, 28, and 15 and 14, respectively. However, because of difficulties in measuring m/e=28 and 29 in our experiment, we used ^{18}O to measure spectra of $C^{18}O^+$ and $CH^{18}O^+$ at m/e=30 and 31.

The m/e=42 data shown in Figs. 1 and 2 originate from a daughter ion produced in the ionization of the vinoxy radical. In the laboratory angular distribution of m/e=42 shown in Fig. 1, the circles represent measured data points, and the dashed line represents a best fit, as discussed below. The error bars correspond to 95% confidence intervals. The maximum count rates were approximately 40 counts/s. For this set of data, drifts in

the detection probability or the beam intensities were accounted for by scaling all measured points to the value at the reference angle which was chosen to be 40° from the direction of the oxygen atom beam which is defined as 0°. Fig. 2 shows TOF data for m/e=42 at four different laboratory angles together with the best fit obtained.

We chose to monitor m/e=42 for channel (1b) even though the parent mass of the vinoxy radical is m/e=43. It was found that the signal at that m/e was significantly lower, namely only about 3% of m/e=42, the major vinoxy radical fragment. M/e=43 distributions were measured and found to be superimposable on the m/e=42 distributions after appropriate scaling. The fact that very little signal (only slightly more than expected from the isotopic abundance of ^{13}C in $C_2H_2O^+$) was found at the parent mass of the vinoxy radical is not surprising since in previous studies using electron impact ionization[43] or photoionization[44] the parent ion of the vinoxy radical could not be detected easily mass spectrometrically.

From the analysis of the part of the angular distributions and TOF spectra arising from fragment ions of the vinoxy radical, it was possible to extract information on its ionizer cracking pattern. This was done for CH_2^+, CH_3^+, CO^+, CHO^+, C_2O^+, C_2HO^+, $C_2H_2O^+$, and $C_2H_3O^+$. For the other masses this was not possible, due to the predominance of nonreactively scattered signal, and the corresponding fragmentation yields for vinoxy radical had to be estimated from comparison with published mass spectra[45] of related

compounds. The mass spectrum of vinoxy radical obtained in this manner is shown in Fig. 3.

In comparing those features of the TOF spectra at different m/e values at a laboratory angle of 35° that correspond to vinoxy radical fragments, we noted that the peak shapes at different masses differed from one another. Particularly in the m/e=15 (CH_3^+) and m/e=31 ($HC^{18}O^+$) spectra (Fig. 4), a distinct dip (as compared to m/e=42, Fig. 2) was found at flight times corresponding to product with very small velocities in the CM frame, or velocities near the velocity of the CM of the system in the laboratory frame. This could be explained if the m/e=42 signal could stem from two different reactive channels, with the vinoxy radical being the predominant source, and a minor product with very low velocity in the CM-frame which corresponds to that part of the m/e=42 signal that is "missing" in the m/e=15 and m/e=31 spectra. A possible minor channel producing signal at m/e=42 is the production of acetyl radical and hydrogen atom from the decomposition of the CH_3CHO intermediate,

$$O(^3P) + C_2H_4 \rightarrow H + CH_3CO \qquad (1g)$$

and will be discussed later. The effect of this minor channel on the determination of the vinoxy fragmentation pattern is small.

The $P(E_T)$ and $T(\theta)$ distributions obtained for channel (1b) are shown in the lower panels of Figs. 5 and 6, respectively. The translational energy distribution, $P(E_T)$, was found to be very

broad, peaking at about 8 kcal/mole and extending to about 30 kcal/mole. The average energy release is about 13 kcal/mole. The CM angular distribution, $T(\theta)$, is almost isotropic but shows a small amount of preferential backward scattering (with respect to the O-atom beam) of the product. These distributions fit both the angular distribution and the TOF-spectra simultaneously, as shown in Figs. 1 and 2. The agreement is good in both cases. By considering the angular distributions and TOF data separately, it was found that an isotropic distribution would actually fit the angular distribution better, whereas the TOF data suggest stronger backward scattering. In any case, the deviations from isotropy are small.

The maximum of the translational energy distribution (lower panel in Fig. 5) of 30 kcal/mole, shown in the lower panel of Fig. 5, which is actually about 7.5 kcal/mole higher than the calculated total available energy using a collision energy of 6.2 kcal/mole and the value of 16.3 kcal/mole for the exothermicity calculated by C. F. Melius.[23] Our data analysis is very sensitive to the shape of the $P(E_T)$ curve at low energies but considerably less sensitive to the distribution at higher energies, therefore no definite conclusion on the value of the exothermicity can be drawn from our data.

In addition, all m/e=42 TOF-spectra show an additional fast component (see Fig. 2). The wider tails in the angular distribution also reflect the existence of this fast component. Reaction of ethylene dimers with oxygen atoms, reactions of trace

amounts of $O(^1D)$, or additional reaction channels, such as (1c), could produce products at velocities on the order of those observed here. Consequently, the fast edge of the m/e=42 features identified with vinoxy radical was somewhat obscured resulting in additional uncertainty in the high energy part of the $P(E_T)$ distribution.

In our search for signal from the products of channel (1a), the formation of methyl and formyl radicals, we relied mostly on the data obtained using ^{18}O in order to be able to distinguish the CO^+ and the CHO^+ signal from the ambient background. However, an additional difficulty lies in the kinematics of this channel. A heavy particle, such as the vinoxy radical, which is recoiling from a very light particle, like a hydrogen atom, has a very small velocity in the CM frame since the CM velocities are inversely proportional to the fragment masses as a result of momentum conservation. A small CM velocity is reflected by an angular distribution that peaks sharply near the angle of the CM in the laboratory frame as seen in the vinoxy distribution, Fig. 1. In an exothermic reaction producing pairs of product molecules with comparable masses, such as CH_3 and CHO, the CM velocities for both products will be large even for small releases of available energy into kinetic energy, resulting in products spread over a wide angular range in the laboratory frame, causing low signal levels at all angles, and only part of the products can be detected within the detector angular range.

The differences in the kinematic relations between the two

channels described above are clearly seen in Fig. 7, which shows contour diagrams of product flux for channels (1a) (upper panel) and (1b) (lower panel). The flux distributions in Fig. 7 represent the final results of the analysis as discussed later.

Because of the difficulties mentioned above, Buss et al.[24] were not able to see evidence for the occurrence of channel (1a). In the present experiment, angular distribution measurements at m/e=30 ($C^{18}O^+$) or 31 ($HC^{18}O^+$) were not attempted, since it was found to be impossible to extract meaningful information from our earlier experiments on the analogous case of the O + C_2H_2 reaction.[39]

The problems of not being able to measure laboratory angular distributions are not very serious, however, since the reaction is expected to go through a long lived complex and TOF data will provide a great deal of dynamical information. Whereas fast and widely scattered products are difficult to discern in angular distribution measurements, fast products are easily identifiable in the TOF spectra, since the signal is accumulated in only a few channels. Fig. 8 shows data at four different angles for m/e=30 using ^{18}O and the upper panel of Fig. 4 shows the TOF spectrum obtained for m/e=31 using ^{18}O at 35°. Two different components can be distinguished in the spectra - the slower one has a shape similar to the m/e=42 spectra and can be identified as a daughter ion of vinoxy radical, and the faster component can be identified as stemming from CHO, the product of reaction channel (1a).

It should be noted that the TOF spectra at 20° and 35° for

m/e=15, 30 and 31 shown in Figs. 4 and 8 were corrected for an experimental artifact which was described in detail in our previous paper[39] and has no effect on the results of the data fitting procedure.

From the analysis of the fast components of the TOF spectra, the $P(E_T)$ and $T(\theta)$ distributions shown in the upper panels of Figs. 5 and 6, respectively, were obtained. The translational energy distribution for channel (1a) again extends out to the total available energy (34 kcal/mole for this channel) with a peak at about 6 kcal/mole (corresponding to 18% of the total available energy) and an average translational energy of about 12 kcal/mole. While the general features of this distribution are well defined by our data, some uncertainty remains in the exact shape, particularly in the high energy part, as a result of noise in the data and incomplete separation of the two components in the m/e=30 and 31 TOF spectra.

The best fit CM angular distribution ($T(\theta)$) shown in the upper panel of Fig. 6 is strongly forward-backward peaked. The condition of symmetry about 90° was imposed, as discussed below, to reflect the existence of a long-lived intermediate. However, since a substantial fraction of products gets scattered outside the detector scanning range, as mentioned earlier, the shape of $T(\theta)$ for channel (1a) is much more uncertain. The effect of the choice of the $T(\theta)$ for this channel on the branching ratio is, in fact, small - if an isotropic CM angular distribution was assumed instead of a forward-backward peaking one, the branching ratio changed only

by about 2%.

We also made an attempt to find the other product of channel (1a), methyl radical, and measured TOF distributions at m/e=15 and 14 at 35°. The spectrum at m/e=14 was dominated entirely by a fragment of nonreactively scattered ethylene, but the spectrum at m/e=15 (lower panel in Fig. 4) clearly shows three different contributions: the slowest part can be identified with a fragment of vinoxy radical (even though the shape is different, as discussed above), the middle feature is due to fragmentation of nonreactively scattered ethylene, and the fastest part possibly corresponds to CH_3 from reaction (1a). The long-dashed line corresponding to the fastest feature in Fig. 4 was calculated using the dynamical information obtained for channel (1a) from an analysis of the m/e=30 data and scaled to fit the experimental data. The comparison between calculation and data suggests that the fast feature is indeed due to CH_3 from channel (1a). However, the intensity derived from the fast feature in the m/e=15 data would correspond to a much larger branching ratio (favoring channel 1a) than calculated from the analysis of the m/e=30 data. Therefore, the fast feature is probably only partly due to this product and partly due to other unidentified sources.

The analysis procedure yields relative total cross-sections σ_a^0 and σ_b^0 for each of the reaction channels through the scaling of calculated distributions to the measured spectra.[46] Since the absolute intensities of the molecular beam, the exact size of the collision volume, and the detection efficiency are not known,

absolute reaction cross-sections can not be directly derived in our experiment. However, these parameters do not change during the course of an experiment, and therefore the branching ratio between two reaction channels can be calculated from the ratio of the relative cross-sections corrected for the ionization cross-sections and fragmentation patterns for the products. The branching ratio R, defined as the ratio of the total reaction cross-sections σ_a and σ_b for channels (1a) and (1b) is obtained as follows:

$$R = \frac{\sigma_a}{\sigma_b} = \frac{\sigma_a^0}{\sigma_b^0} \times \frac{Q_{vinoxy}}{Q_{CHO}} \times \frac{f_{vinoxy}^{42}}{f_{CHO}^{30}} .$$

Here σ_a^0 and σ_b^0 are the apparent cross-sections derived from the signal at m/e=30 and 42, Q_{vinoxy} and Q_{CHO} are the ionization cross-sections approximated using the method of Fitch and Sauter[47] and f_{CHO}^{30} and f_{vinoxy}^{42} are the fractions of $HC^{18}O$ and C_2H_3O which yield ions of m/e=30 and 42, respectively, upon ionization. The mass spectrum of CHO and the vinoxy radical (Fig. 3) were constructed from angular distributions and TOF data for major fragments and from estimates of minor fragments using the well known mass spectra of related compounds.[45]

The TOF measurements at different angles were performed under slightly different conditions, but great care was taken to check the experimental conditions by frequently alternating between the different products monitored. In this case we had to switch between ^{18}O and ^{16}O. The number densities for both beams were

found to be identical. A value for R was thus calculated for the data at 20°, 35°, 45° and 55° separately. The results are R(20°)=2.4, R(35°)=2.9, R(45°)=2.4, and R(55°)=2.5.

Three main sources contribute to the error in the determination of the branching ratio. The experimentally derived quantity σ_a^0/σ_b^0 contains errors due to fluctuations in the detection efficiency and errors due to uncertainty in the $P(E_T)$ and $T(\theta)$ distributions, particularly for channel (1a). The overall error of σ_a^0/σ_b^0 is estimated at about 25%. The correction factor Q_{HCCO}/Q_{CO} is estimated to be reliable to about 20% since an empirical method was used[47] whose applicability to polyatomic radicals has not been tested. The fragmentation patterns for C_2H_3O and CHO were measured, but are associated with the same uncertainties all quantitative measurements in our system carry. The uncertainty of the factor $f_{vinoxy}^{42}/f_{CHO}^{30}$ is estimated to be about 20% as well. The overall result for the branching ratio R is therefore 2.5±0.9.

Discussion

The results of our crossed molecular beam experiment clearly demonstrate the occurrence of the two major reaction channels (1a) and (1b). Channel (1b) has been identified in previous crossed molecular beam experiments[24-26] and confirmed repeatedly since. In this new investigation, we were able to observe channel (1a) under single collision conditions. Thus the apparent discrepancy between

bulk phase studies and molecular beam experiments has been resolved.

The finding that vinoxy radical undergoes extensive fragmentation upon electron impact ionization provides a possible explanation for earlier results where ketene was thought to be a major product[20,21] based on the appearance of product peaks at m/e=42. In addition, signal at m/e=15 and 29 could be due to either the products of channel (1a) or fragments of vinoxy radical, and m/e=29 could also represent some $C_2H_5^+$ from the fast reaction of hydrogen atoms with ethylene in the high pressure reactors.[48]

The analysis of our experiment did not yield absolute cross sections, but only the ratio of the relative cross sections for channels (1a) and (1b), which was found to be 2.5±0.9. Under the assumption that no other reaction channel contributes, this would correspond to 71% (62-77%) of the reaction following channel (1a) and 29% (23-38%) following channel (1b). It is not clear to what extent the use of ^{18}O affects the rate of ISC and thus the branching ratio. However, it appears to be established that channels (1a) and (1b) are the major ones under conditions of relatively small collision energies or low temperatures. In several recent investigations, absolute branching fractions for either channel (1a) or (1b) have been obtained (see Table I). Our results are in qualitative agreement with these recent measurements. It is important to note that no indication of a significant pressure dependence of the branching fractions was found in previous investigations and that the crossed molecular

beam results presented here confirm that both processes (1a) and (1b) are indeed primary reaction steps and not a consequence of secondary collisions of reaction intermediates.

The temperature dependence of the branching ratio was only studied by Smalley et al.[36] who found a slight decrease (i.e., more H production) at temperatures up to 769 K. We did not measure the dependence of the cross section and the branching ratio on collision energy. The collision energies used in the present experiment were much higher than those in a thermal experiment, but the internal excitation of the reaction intermediate only corresponds to that created by reactants at around 700 K.

A large amount of theoretical work has been done on both the triplet and singlet C_2H_4O potential energy surfaces. This information greatly facilitates understanding experimental results. Fig. 9 schematically shows parts of the triplet (solid lines) and singlet (dashed lines) C_2H_4O surface taken mainly from calculations by C. F. Melius.[23]

The $O(^3P)$ atoms follow an out-of-plane approach during which the CCO-plane constitutes the plane of symmetry.[49] The reaction leads, via a small entrance channel barrier, to a triplet diradical CH_2CH_2O. There actually exist two pairs of states of this diradical with very similar energies (lying within a few kcal/mole),[49,50] where the two states in a pair can interconvert by rotation about the C-C bond with a barrier of only about 0.6 kcal/mole.[50] As indicated in Fig. 9, the approach following A" symmetry leads to the lower pair of states, whereas the approach

following A' symmetry leads to the higher lying pair. Diradicals in the two lower energy states can react along several different pathways, e.g. elimination of a hydrogen atom to form vinoxy radical or 1,2-H migration to form triplet acetaldehyde which in turn would dissociate, with barriers of several kcal/mole, to CH_3 and CHO. It was suggested[28] that the energetically higher lying pair of states can either react to form the first excited electronic state (A^2A') of vinoxy radical or undergo ISC. The (A^2A') state was found to be 23 kcal/mole higher in energy than the ground state (X^2A'')[28] and is therefore energetically inaccessible in our experiment.

The pathway forming (ground state) vinoxy radical in our experiment shows a maximum release of translational energy approximately equal to the calculated available energy (lower panel in Fig. 5). In addition, the fact that the distribution peaks well away from zero is indicative of an exit channel barrier[51] which is in agreement with the calculations as well. The CM angular distribution $T(\theta)$ found in our experiment is not completely isotropic or forward-backward symmetric. These results could suggest that the life time of the triplet diradical is not much longer than a rotational period.

The translational energy distribution obtained from the analysis of the present experiment is in agreement with distributions found in earlier molecular beam experiments: Baseman[52] reported $P(E_T)$ functions for channel (1b) at nominal collision energies of 5.4 and 8.3 kcal/mole, respectively, which

display essentially the same features as the one reported here. Clemo et al.[26] reported a distribution with a broad peak at around 11 kcal/mole and a sharp cutoff at 19 kcal/mole. Baseman[52] found that the experiment at 8.3 kcal/mole collision energy could be fit using CM angular distributions $T(\theta)$ with sideways or slight forward peaking. Clemo et al.[26] reported a $T(\theta)$ that was close to isotropic but slightly favored forward scattering.

In contrast to channel (1b), the formation of CH_3 and CHO, channel (1a), is an unlikely process on the triplet potential energy surface, since a 1,2-hydrogen migration in the diradical intermediate has a prohibitively high barrier according to ab initio calculations. The results of C. F. Melius[23] place this barrier at about 9 kcal/mole above the total available energy in our experiment. Tunneling corrections could not explain the high rate of reaction. The fact that channel (1a) is greatly enhanced in the case of the $O(^3P) + C_2D_4$ reaction[53] indicates that tunneling is not responsible. Only rapid ISC from a triplet to a singlet diradical can explain the observations. On the singlet surface, there is no barrier expected for the 1,2-H migration to form ground state (singlet) CH_3CHO and also no significant exit channel barrier for the C-C bond rupture is expected to form CH_3 + CHO.[54]

For a simple bond rupture reaction of a polyatomic molecule without an exit channel barrier, a translational energy distribution peaking at zero energy would be expected. The $P(E_T)$ distribution we obtained for channel (1a) (upper panel in Fig. 5) shows a peak at about 6 kcal/mole which represents a relatively

small fraction (18%) of the total available energy, but clearly does not correspond to a typical simple bond rupture case. A possible explanation for this phenomenon arises from the release of some of the rotational energy of the reaction intermediates into the translational energy of products. The orbital angular momentum, $J=24\hbar$, corresponding to the impact parameter of approximately 0.7Å (obtained from the geometry of the transition state, Ref. 49) is the main source of rotational angular momentum of the complex. In the process of C-C bond rupture after H-migration, some fraction of the rotational energy of the complex is expected to be converted into translational energy of the fragments. However, since the exit impact parameter is expected to be much larger than the impact parameter of the reactants, no more than 1.0 kcal/mole of translational energy will come from the rotational energy of the reaction intermediate, and this can not explain the peak of the $P(E_T)$ at 6 kcal/mole. Therefore there is a possibility of a small exit channel barrier for this C-C bond rupture process. On the other hand, if all the angular momentum of the complex is converted into orbital angular momentum of the products, a minimum of about 6 kcal/mole is expected to be released as translational energy.

The comparison of these results with the $O(^3P)$ + acetylene reaction shows that the translational energy distributions for the $O + C_2H_4 \rightarrow CH_3 + CHO$ and the $O + C_2H_2 \rightarrow CH_2 + CO$ channels are qualitatively different; in the latter case a broader distribution peaking at 27% of the total available energy was found,[39]

indicating a relatively large barrier. The barrier for C-C bond rupture in $^3CH_2CO$ was calculated to be about 34 kcal/mole.[23,55] The acetylene reaction, in contrast to the ethylene case, is indeed thought to proceed mostly on the triplet surface.[55]

For channel (1b), we imposed forward-backward symmetry on the center-of-mass angular distribution $T(\theta)$ (upper panel of Fig. 6), which corresponds to the assumption that the precursor of CH_3 + CHO, presumably $^1CH_3CHO$, has a lifetime significantly longer than a rotational period, estimated to be about 2ps. Even though this is not an unambiguous result of the data analysis, the data for channel (1a) were found to be compatible with this assumption. It is supported by the conclusion of Bley et al.[16] that the lifetime of the addition complex, which is being stabilized to acetaldehyde at high pressures, is of the order of 10^{-11}s. It is possible that the decay of the triplet diradical through the competition of H-elimination and ISC takes place on a time scale shorter than or on the order of a rotational period, while the lifetime of $^1CH_3CHO$ formed through ISC and H-migration is considerably larger.

The energies of the four triplet diradical states considered by Dupuis et al.[49] and Yamaguchi et al.[50] were found to be very similar to those of the four singlet diradicals. More recent results[54] indicate a singlet state lying about 12 kcal/mole lower than the triplet diradical. It was suggested[50] that ISC would be facile in this system since spin-orbit coupling should be efficient due to the orthogonality of the p-type orbitals in the diradical. Recent unpublished results (Ref. 26 in Ref. 38) indicate that the

two surfaces indeed come close to each other at some points along the reaction coordinate, facilitating the conversion. However, no ISC rates have been calculated.

Apart from the two major reaction channels (1a) and (1b) discussed above, several other exothermic pathways are possible. Vibrationally hot adduct, acetaldehyde or ethylene oxide, could only be considered as a reaction intermediate in our experiment; RRKM calculations[56] indicate that without stabilization through collisions, none of these highly excited molecules could survive for several hundred microseconds to reach the detector in our experiment.

The formation of formaldehyde and triplet methylene, channel (1d), was found to account for 6±3% of the products by Bley et al.[16] using LMR detection of CH_2 radicals. Endo et al.[38] found that CH_2O was formed mainly by secondary reactions, but possibly a small amount was being formed in a primary reaction step. Peeters and Vinckier[57] suggested that reaction (1d) is the predominant source of CH_2 in ethylene flames. According to theory[23] (Fig. 9), the barrier for CH_2-elimination from the triplet diradical is about 9 kcal/mole higher than that for H-elimination to form vinoxy radical. From this the ratio of reaction (1d) to (1b) is expected to be quite small. In our experimental data, no evidence was found for the occurrence of this channel. A small amount of CH_2O may have gone undetected, however.

The formation of ketene and molecular hydrogen, reaction (1c), although not considered to be a major channel in the recent

literature, deserves some consideration. On the triplet surface, ketene could be formed by 1,1-H_2-elimination from the diradical. Such elimination processes typically have substantial barriers. However, in this particular case the barrier could be exceptionally low in view of the comparatively low barrier for H-elimination.[23] To our knowledge, no theoretical calculation has been undertaken for this special case. Even if the barrier is several kcal/mole higher than that for H-elimination, a certain fraction of the molecules could react according to this pathway.

Another pathway to ketene proceeds through the singlet diradical. In this case, again, no ab initio calculations are available that could answer the question of the existence and magnitude of a barrier for the 1,1-H_2-elimination process. However, Melius' calculations show a possibility that this process occurs with at most a very small barrier on the singlet surface.[58] The alternative route, the 4-center H_2-elimination from acetaldehyde, is expected to have a very high barrier. If it does not greatly exceed the threshold for C-C-bond rupture, then 1,2-H_2-elimination has to be considered as a minor reaction pathway. In Fig. 9 this possibility is indicated.

The question arises, whether the signal that we attribute to vinoxy radical could be partly or entirely due to the formation of ketene. Considering first the triplet case, from the estimated exothermicity,[59] which is 18 kcal/mole larger than that for the H + vinoxy channel, and the likely existence of a barrier, we would expect a considerable translational energy release. These

assumptions could not fit the m/e=42 data. In addition, the component of the signal at m/e=15 (CH_3^+) which shows essentially the same features as the m/e=42 distributions, could not be explained by invoking this channel. Furthermore, spectroscopic identification[27,28,32] leaves no doubt that vinoxy indeed occurs as a major primary product in the $O(^3P) + C_2H_4$ reaction. However, the possibility can not be excluded that a small fraction of our m/e=42 signal is due to ketene.

In the case of the reaction forming ketene on the singlet surface where more energy will be available, an even larger release of translational energy is expected if the dynamics is determined by repulsive forces. As a result, this channel would be expected to manifest itself in very fast components in the TOF spectra. Such fast components were indeed found in the m/e=42 spectra, and they are possibly in part due to the formation of ground state ketene and molecular hydrogen. However, without further experiments, this assignment can not be made with certainty.

Additional pathways that are conceivable are the formation of hydrogen atom and acetyl radical, CH_3CO - channel (1g) - or hydrogen atom and vinoxy radical via the singlet surface, i.e. as dissociation products of highly vibrationally excited acetaldehyde. Simple RRKM calculations[56] indicate that the ratio (CH_3 + CHO):(CH_3CO + H):(CH_2CHO + H) would be about 1:0.05:0.0025. These numbers strongly depend on the values for the dissociation thresholds, but it is likely that a small amount of acetyl radical is formed. Because the process is a simple bond rupture, a small

amount of translational energy is expected in the fragments. In fact, the different shapes of the relevant parts of the m/e=42, 15, and 31 data as discussed above strongly suggest two separate sources of m/e=42 product. Thus, that part of the m/e=42 signal which corresponds to very low velocities in the center-of-mass frame and which is partly absent in the m/e=15 spectra could be due to acetyl radical. So far, acetyl has escaped spectroscopic detection in the O + ethylene reaction, possibly because the radical lacks accessible electronic transitions.[60]

This clearly does not exhaust the list of thermodynamically possible channels in the C_2H_4O system. For instance, Donaldson and Sloan[61] suggested the channel

$$O(^3P) + C_2H_4 \rightarrow [C_2H_4O]^{\ddagger} \rightarrow H + CO + CH_3 \qquad (1h)$$

as a possible source of vibrationally excited CO.

It is also of interest to compare the products of the $O(^3P)$ + C_2H_4 reaction with the products of the photodissociation of acetaldehyde. If internal conversion of the initially prepared electronically excited state is fast, then the products of photodissociation and of chemically activated acetaldehyde at similar excitation energies should be similar. The photodissociation of acetaldehyde has been studied extensively[62] in the wavelength region 240-340 nm. Three reaction channels have been observed:

$$CH_3CHO \xrightarrow{h\nu} CH_3 + CHO \qquad (2a)$$

$$CH_3CHO \xrightarrow{h\nu} CH_3CO + H \qquad (2b)$$

$$CH_3CHO \xrightarrow{h\nu} CH_4 + CO \qquad (2c)$$

Channels (2a) and (2b) correspond to channels (1a) and (1g), respectively, but channel (2c) has no equivalent in the $O(^3P)$ + C_2H_4 reaction, since CH_4 was not detected among the major products in any previous experiment. It is questionable, however, whether channel (2c) constitutes a primary reaction channel at all, since the barrier for this process was calculated to be 8 kcal/mole above the dissociation threshold for $CH_3CHO \rightarrow CH_3 + CHO$.[63]

Future research is expected to shed more light on minor reaction channels. At this point, it appears that a consensus has been reached on the mechanism and the identity of the primary products of the $O(^3P)$ + C_2H_4 reaction.

A fairly thorough understanding of these reactions is of central importance for the description of complex combustion systems. The inclusion of channel (1b) in model calculations might have important effects since an additional source of H atoms is introduced. Although a large amount of spectroscopic information is available for the vinoxy radical,[27,32,60,64] its application to direct measurements of concentration profiles in complicated systems has not been developed so far. At present, little is known about reactions of vinoxy radical, except for its reaction with molecular oxygen.[65]

Conclusions

Using the crossed molecular beam technique, the occurrence of two major channels in the reaction of ground state oxygen atoms and ethylene under single collision conditions was confirmed, namely formation of methyl radical and formyl radical (channel (1a)) and formation of hydrogen atom and vinoxy radical (channel (1b)). Upon formation of a triplet diradical from the addition of $O(^3P)$ to ethylene, two competitive processes of approximately equal importance are responsible for the fast decay of the triplet diradicals. One of the processes is the direct elimination of a hydrogen atom to form vinoxy radicals and the other is ISC from the triplet to a singlet diradical. Most of the singlet diradicals are first transformed into highly vibrationally excited acetaldehyde through 1,2-H migration and then decay into products in a time much longer than the rotational period of 2 ps. The vibrationally excited singlet acetaldehyde then decays mostly into CH_3 and CHO. A value for the branching ratio σ_a/σ_b of 2.5±0.9 was determined which is in approximate agreement with other recent determinations.

In addition to these two major channels, our experiment also provides evidence for the formation of acetyl radical and hydrogen atoms, a minor dissociation channel from vibrationally excited CH_3CHO. Furthermore there is possibly a minor channel forming ketene on the singlet potential energy surface.

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Table I: Recent experiments on the relative contributions of channels (1a), (1b), and (1d).

Ref.	%(1a)	%(1b)	%(1d)	total pressure	method
28	52-58	36±4	-	40-760 Torr	photochemical modulation spectroscopy
36	-	27±5	-	50-100 Torr	resonance fluorescence
37	-	79±14	-	0.4-6 Torr	resonance fluorescence
38	50±10	40±10	-	30 mTorr	microwave spectroscopy
16	44±15	50±10	6±3	3-53 Torr	LMR, ESR

Figure Captions

Fig. 1 Laboratory angular distribution for products at m/e=42 ($C_2H_3O^+$). Angles are measured from the oxygen atom beam. Scattered points: measured data points; dashed line: fit.

Fig. 2 Time-of-flight spectra for products at m/e=42 ($C_2H_3O^+$) at four different laboratory angles. Scattered points: data; solid lines: fits, scaled to the data for each angle separately.

Fig. 3 Mass spectrum determined for the vinoxy radical.

Fig. 4 Time-of-flight spectra for products at m/e=31 ($HC^{18}O^+$) and m/e=15 (CH_3^+) at 35°. Upper panel: m/e=31. Scattered points: data; dashed lines: fits for components due to channel (1a), large dashes, and channel (1b), small dashes; solid line: sum of the fits for channels (1a) and (1b). Lower panel: m/e=15. Scattered points: data; dashed lines: fits for components due to channel (1a), large dashes, and channel (1b), small dashes; dash-dotted line: contribution of nonreactively scattered ethylene; solid line: sum of the fits for channels (1a) and (1b) and nonreactive scattering contribution. Calculated curves and nonreactively scattered contribution are scaled to the data for each angle and each channel separately.

Fig. 5 Translational energy distributions, $P(E_T)$, for channels (1a) and (1b).

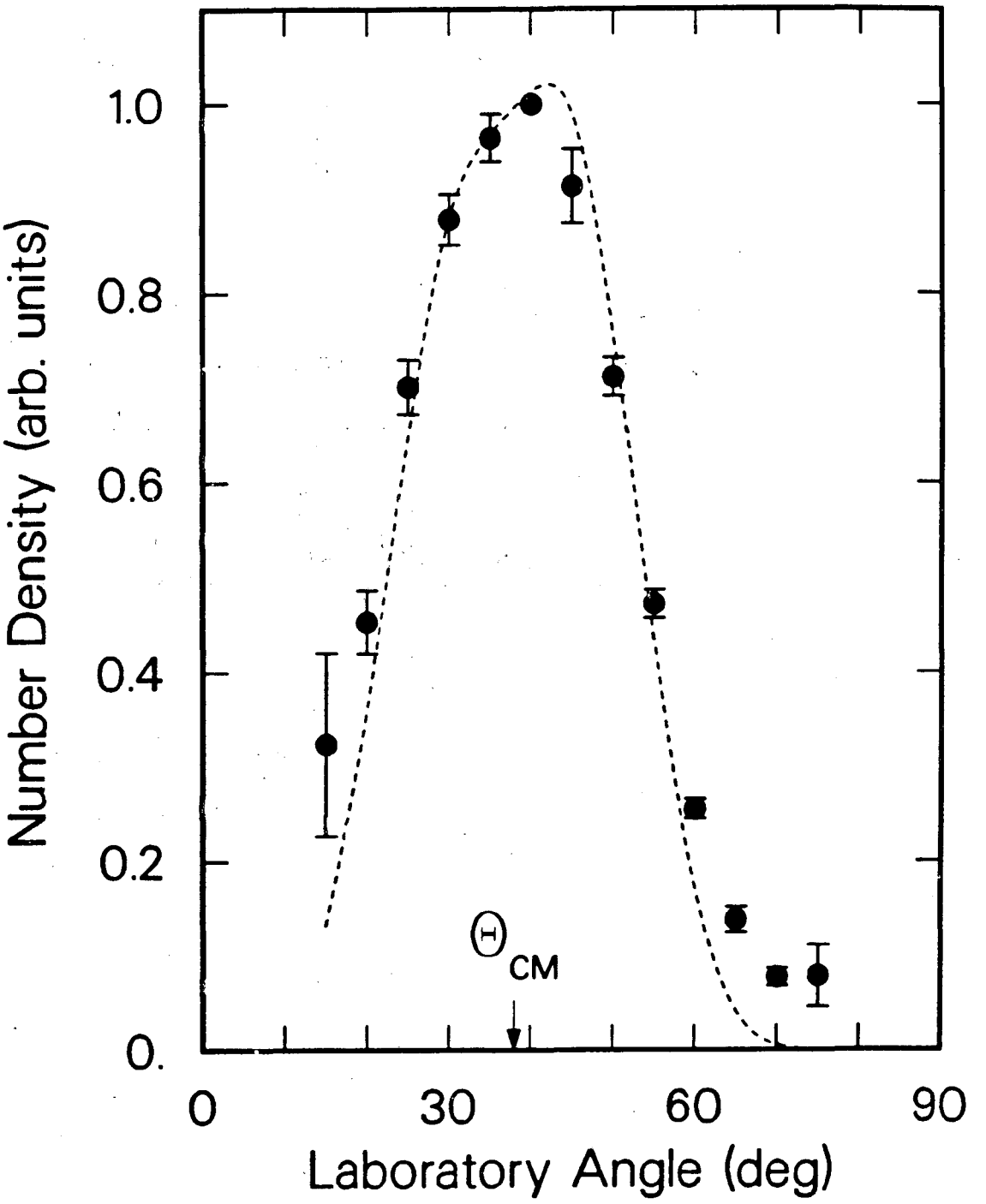
Fig. 6 Center-of-mass angular distributions, $T(\theta)$, for channels

(1a) and (1b).

Fig. 7 Newton diagrams of beam velocities and contour diagrams of product flux for channels (1a), upper panel, and (1b), lower panel.

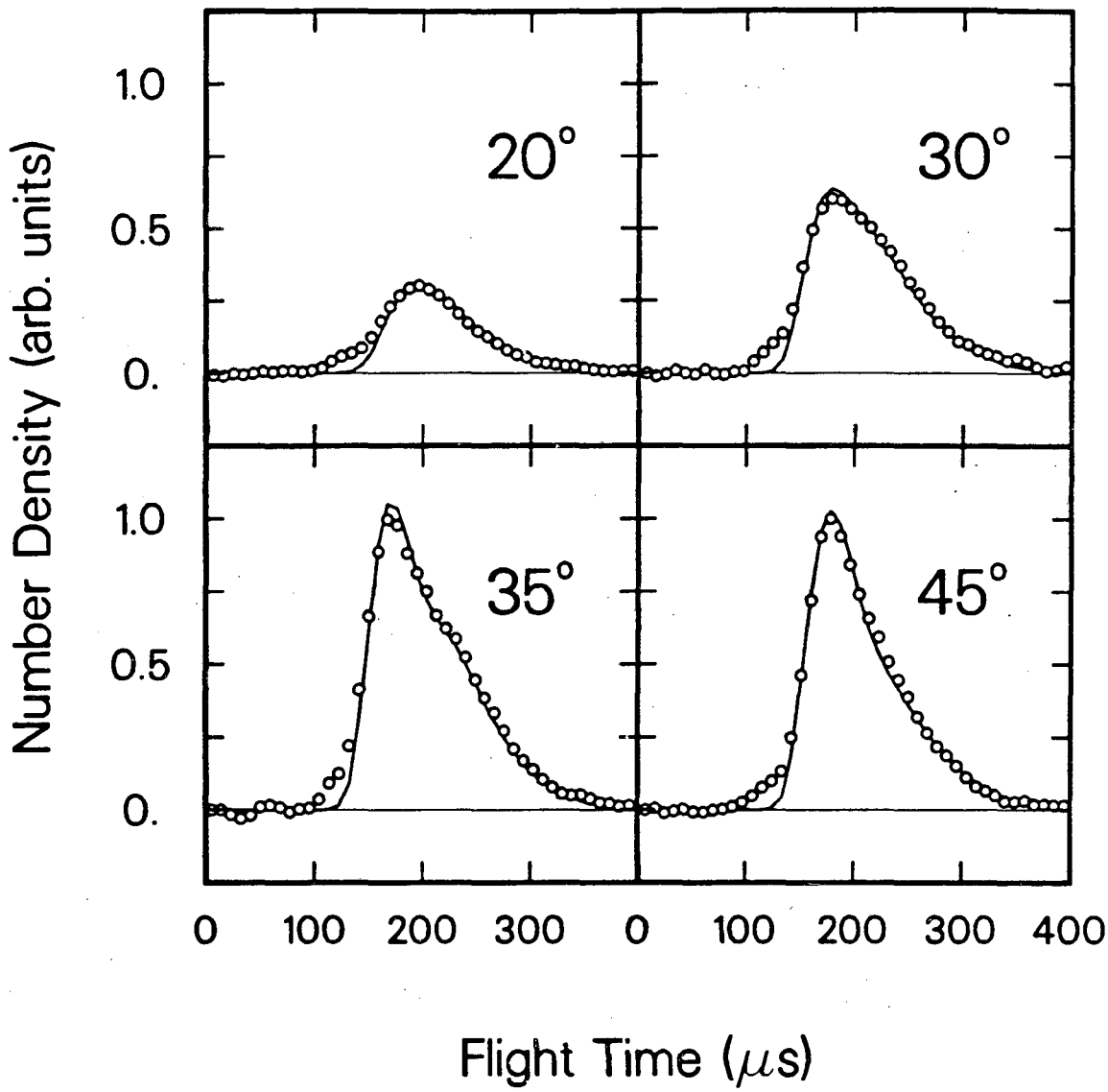
Fig. 8 Time-of-flight spectra for products at m/e=30 ($C^{18}O^{+}$) at four different laboratory angles. Scattered points: data; dashed lines: fits for components due to channel (1a); dotted lines: fits for components due to channel (1b); solid lines: sum of the fits for channels (1a) and (1b). Calculated curves are scaled to the data for each angle and each channel separately.

Fig. 9 Schematic energy diagram for the reaction of $O(^{3}P)$ with ethylene. Solid lines: triplet surface; dashed lines: singlet surface.



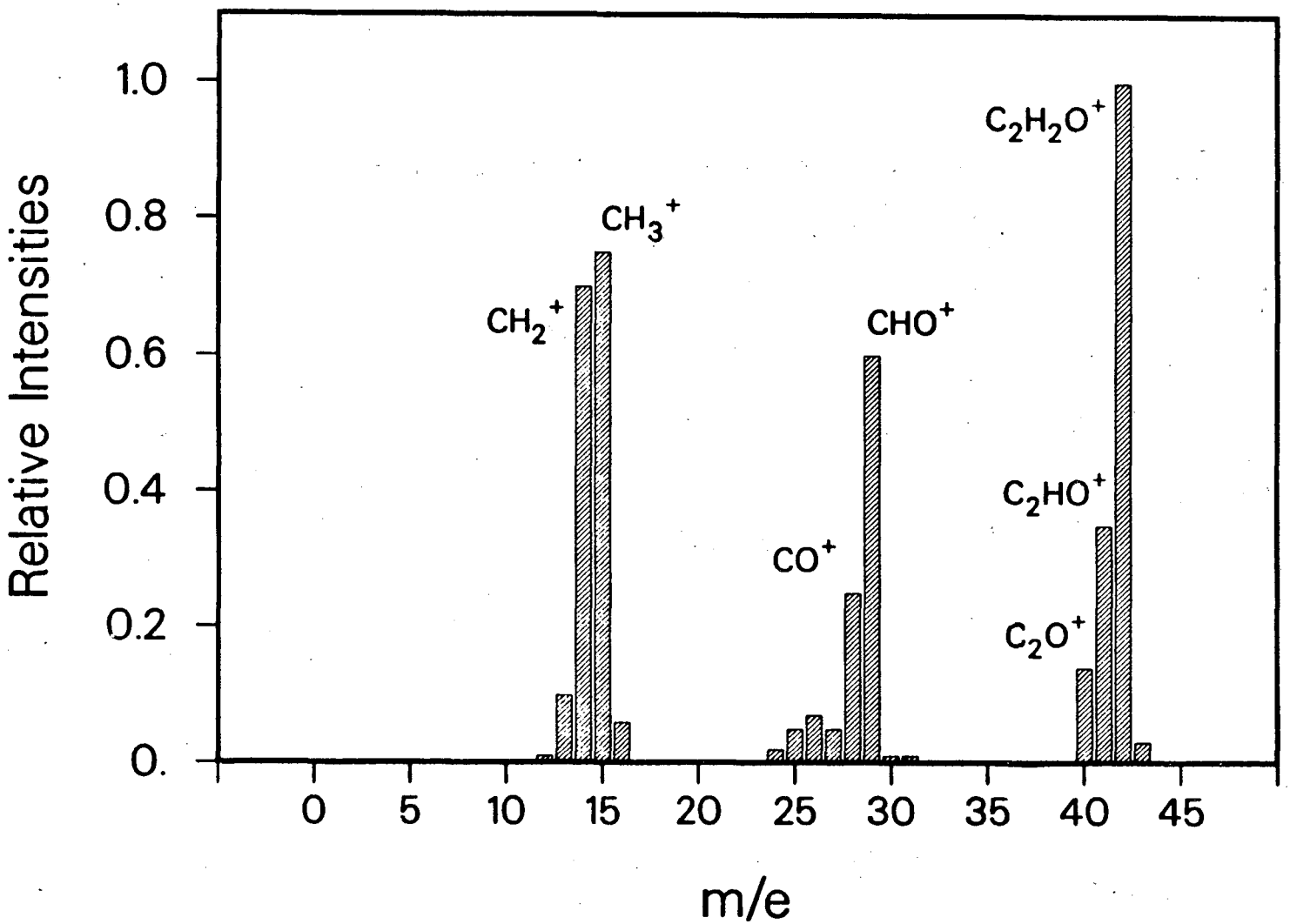
XBL 896-2106

Fig. 1



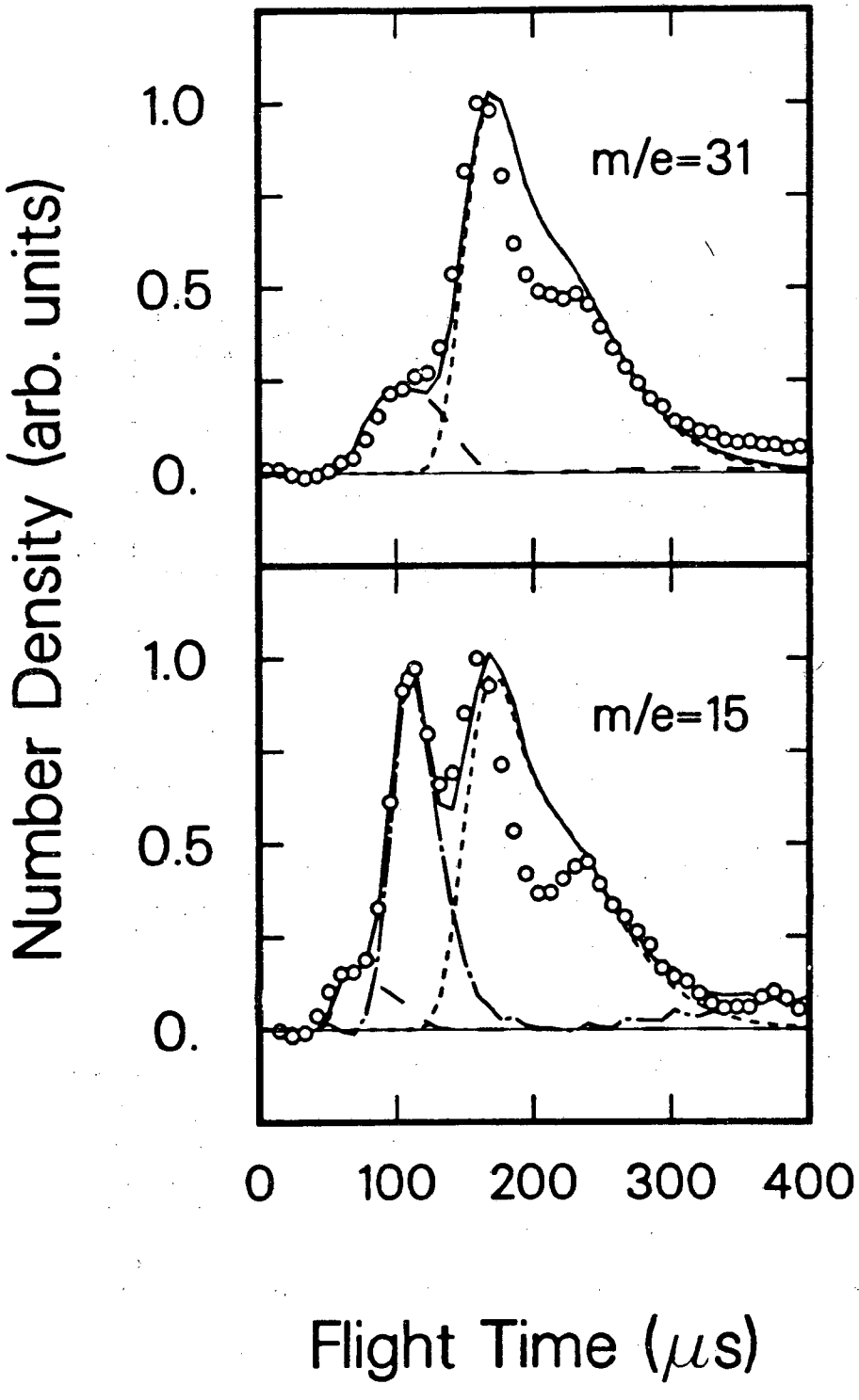
XBL 896-2107

Fig. 2



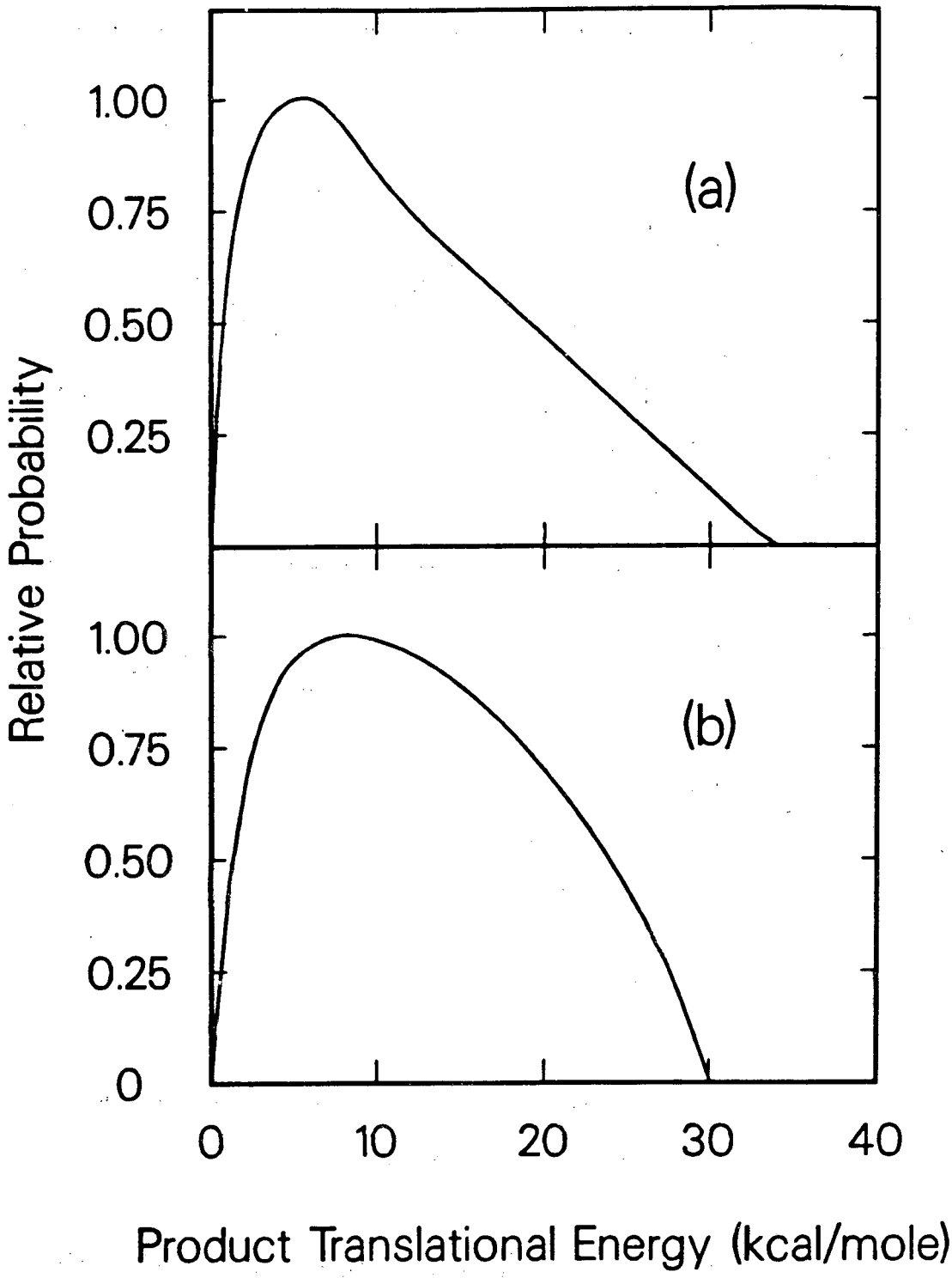
XBL 896-2111

Fig. 3



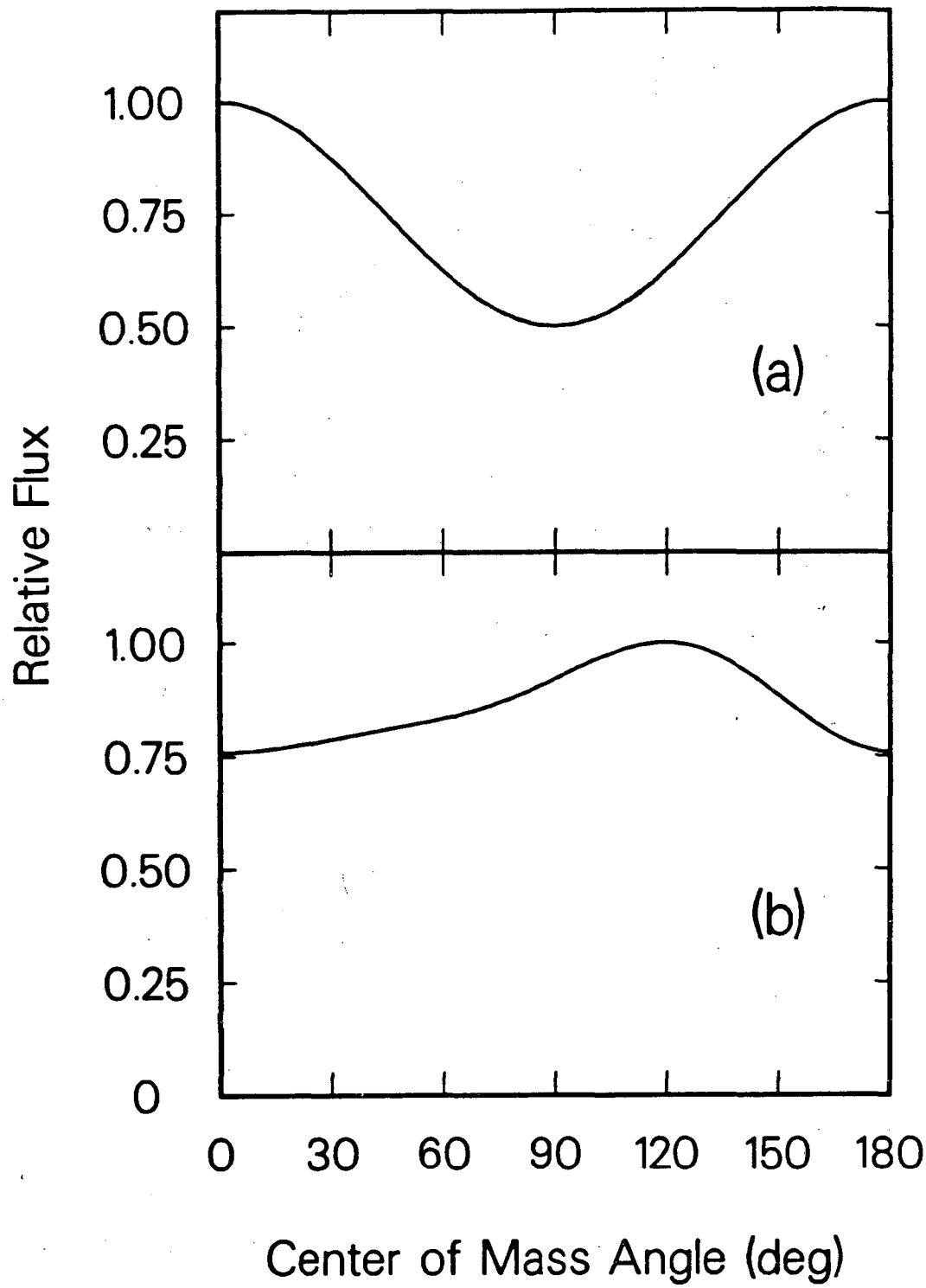
XBL 896-2108

Fig. 4



XBL 896-2113

Fig. 5



XBL 896-2112

Fig. 6

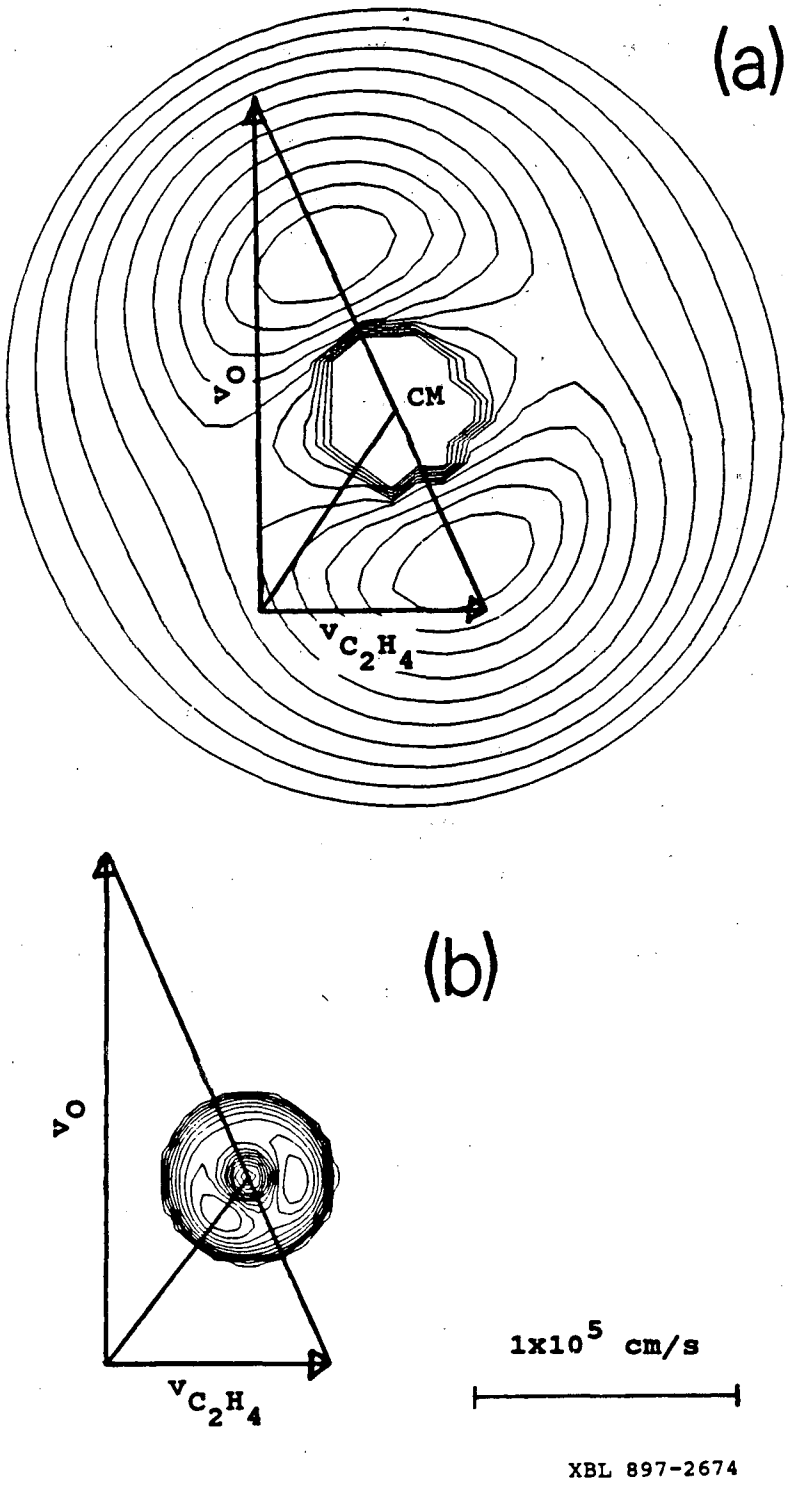
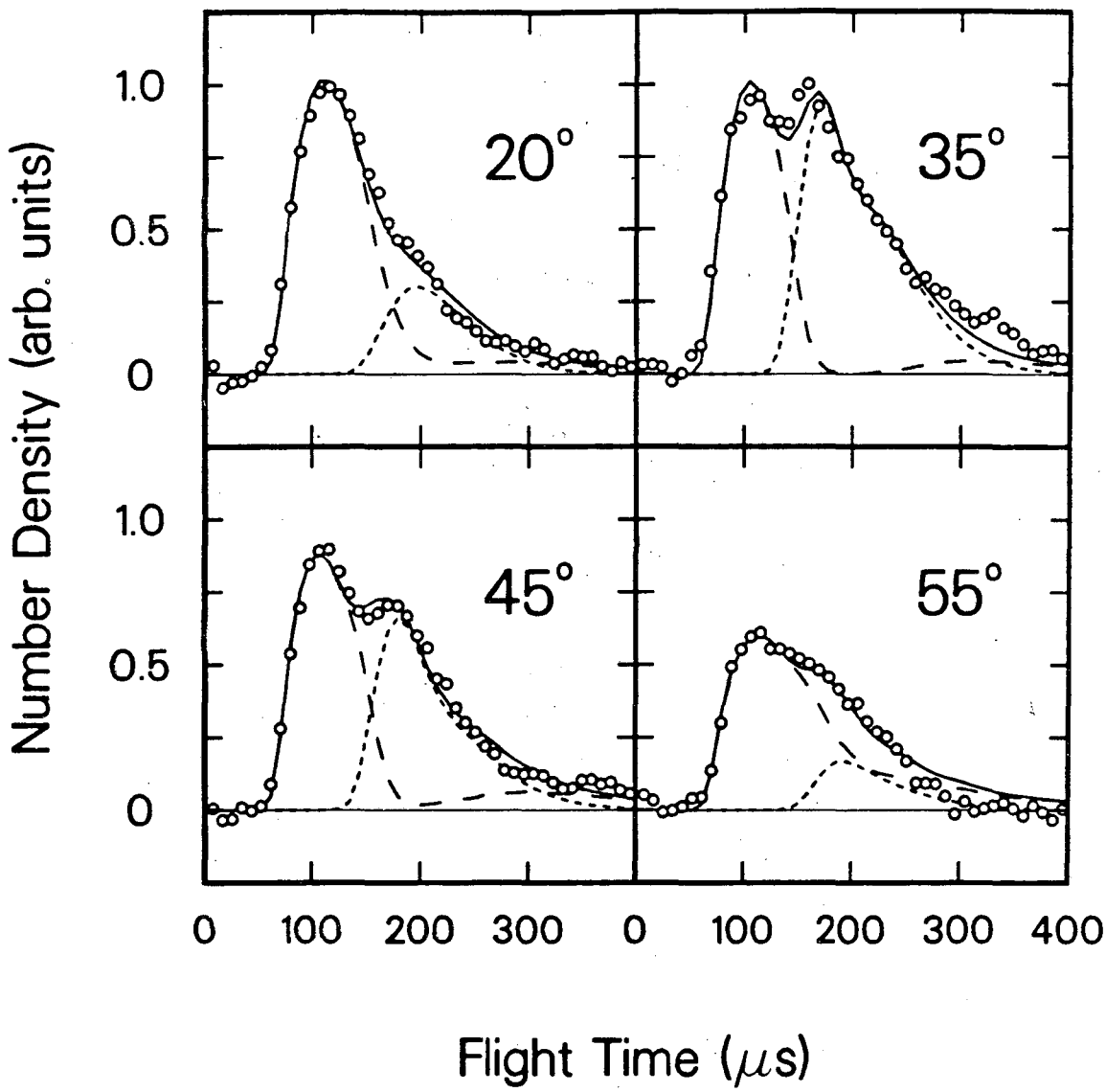


Fig. 7



XBL 896-2109

Fig. 8

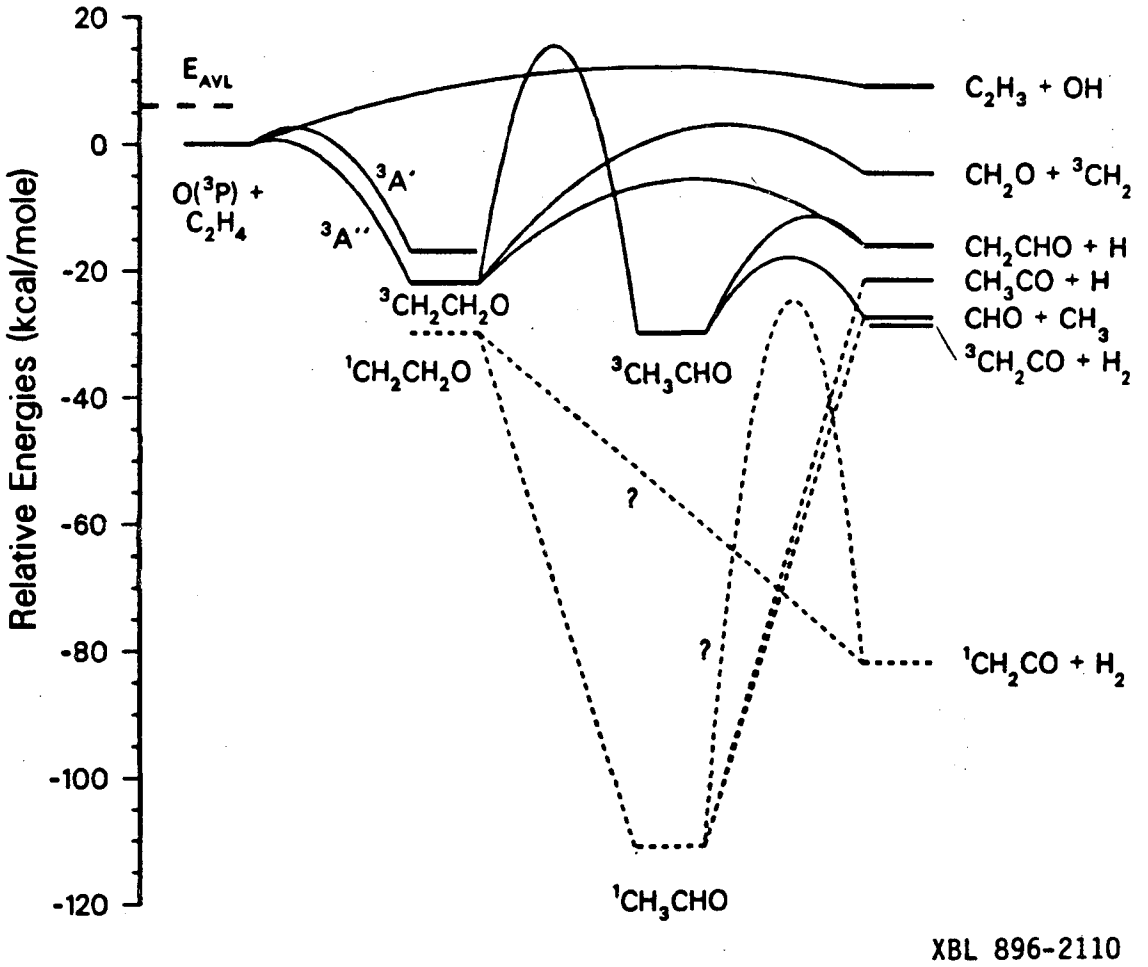

20
0
-20
-40
-60
-80
-100
-120
Relative Energies (kcal/mole)
E_AVL
O(³P) + C₂H₄
³A'
³A''
³CH₂CH₂O
¹CH₂CH₂O
³CH₃CHO
¹CH₃CHO
?
?
C₂H₃ + OH
CH₂O + ³CH₂
CH₂CHO + H
CH₃CO + H
CHO + CH₃
³CH₂CO + H₂
¹CH₂CO + H₂
XBL 896-2110

Fig. 9

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