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Pyrolysis of Styrene. Kinetics and Mechanism of the Equilibrium Styrene \leftrightarrow Benzene + Acetylene

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The thermal unimolecular decomposition of styrene into benzene and acetylene, $C_6H_5CH=CH_2 \rightarrow C_6H_6 + HCCH$ (1), was investigated in a low pressure ($\approx 10 \text{ mTorr}$) flow reactor by on-line mass spectrometry between 1180 and 1350 K. Measured rates can be calculated, via RRKM extrapolation, from the expression log ($k_{1\infty}$, s⁻¹) = 14.38 - 17 076/T, which was derived by detailed balance from high-pressure ($\approx 50 \text{ Torr}$) low-temperature (878-973 K) kinetic data for the reverse reaction. This value of $E_{1\infty} = 77.9 \text{ kcal/mol allows for the generation of vinylidene, H₂C=-C;, the carbene isomer of acetylene, as a primary product of the title reaction. A non-radical process involving the rate-determining extrusion of H₂C=-C; from a [4.1.0]-7-methylene cyclohepta-2,4-diene intermediate in equilibrium with styrene is consistent with kinetic and thermochemical considerations.$

Introduction

The kinetics and mechanism of the thermal isomerization and decomposition of the multitude of C_8H_8 isomers is a fascinating subject.¹ Benzene and acetylene are ultimately formed via non-radical processes through a maze of polycyclic intermediates. Thus for example, the low-temperature pyrolysis of cubane, the most exergonic isomer, leads to highly excited cyclooctatetraene with an activation energy of 43 kcal/mol.² This value, some 40 kcal/mol smaller than the dissociation energy of a normal C–C bond or about 25% of the cubane strain, militates against a biradical intermediate preserving the structure of the original molecular cage. The dissociations of hot cyclooctatetraene and styrene photoexcited at 193 nm also adhere to this pattern: a common bicyclic [4.2.0] isomer lies at the gateway of their exit channels.³

We have recently investigated the mechanism of the thermal dimerization of acetylene below 1000 K, reaching the conclusion that occurs by prior isomerization of HCCH into $H_2C=-C$;, followed by fast addition of this species to a second HCCH molecule.⁴⁻⁸ A similar scheme was thought to apply to the association of acetylene with benzene, which proceeds at similar rates.⁴ Since styrene is the most stable isomer of the C₈H₈ manifold, i.e., the final product of the HCCH + C₆H₆ reaction at high temperatures, we decided to confirm the nonradical nature of these processes and perhaps the participation of vinylidene by examining whether the rates of styrene one-step dissociation into benzene and acetylene and its reverse satisfy detailed balance.^{9,10}

In this paper we report results showing that (1) the kinetics of acetylene decay in $C_6H_6/HCCH$ mixtures can be quantitatively accounted for by known bimolecular reactions, i.e., without invoking free monoradical chains, and (2) the rates of reaction -1 thus derived can be used, in conjunction with independent thermodynamic data, to obtain a high-pressure Arrhenius expression for reaction 1 that accurately reproduces present measurements on the pyrolysis of styrene. The fact that reaction 1 demonstrably occurs in one chemical step definitely rules out free-radical chain mechanisms for the title equilibrium. We found that the activation energy of reaction 1 is compatible with the formation of vinylidene, a condition that also applies to the reported kinetic and thermodynamic data for the thermal elimination of acetylene from barrelene, the [2.2.2] bicyclic isomer of styrene,¹¹ and vinylacetylene.^{6,8} On this basis we discard concerted processes involving closed-shell HCCH. Finally, we show that thermochemical considerations also exclude biradical intermediates in reaction 1.

Experimental Section

A steady flow of styrene vapor $(2 \times 10^{14}-2 \times 10^{15} \text{ molecules} \text{ cm}^{-3} \text{ s}^{-1})$ circulated through a heated, fused silica reactor (volume = 90 cm}^{-3}) at pressures below 10 mTorr. Mixtures of reactant and products effused into the differential chamber of a modulated beam mass spectrometer (Extrel) for on-line analysis. Under such conditions, secondary reactions are effectively suppressed and labile intermediate species, such as free radicals, can be consistently detected. Further details of this technique can be found in previous publications from this laboratory.¹³ The dynamic parameters of the reactor used were: $k_{e,M} = 0.214(T/M)^{1/2} \text{ s}^{-1}$ (escape rate constant of a species of mass *M*, in daltons) and $\omega_M = 4530 \cdot (T/M)^{1/2} \text{ s}^{-1}$ (gas-wall collision frequency); they were routinely checked by measuring the rates of ethylbenzene decomposition, which are known with considerably certainty.¹⁴ Temperatures



Figure 1. Open circles: decay of acetylene in mixtures: $[C_2H_2]_0 = 1.04 \times 10^{-4} M$, $[C_6H_6]_0 = 8.44 \times 10^{-4} M$, T = 946 K. Solid line: calculated from a mechanism comprising reactions -1, 2, 3, and 4 (see text).

were determined by means of two calibrated Pt-10% Rh/Pt thermocouples located at the top and bottom of the reactor.

Mass spectrometric analysis was performed using electron impact ionization at 30 eV. It was complemented by time-of-flight measurements for the different fragment signals, taking advantage of the fact that phase shifts ϕ_i are functions of the masses of the fragment, m_i , and its parent ion \mathcal{M} :^{13,15}

$$\phi_i = a + bm_i^{1/2} + c(M/T)^{1/2} \tag{I}$$

Higher pressure experiments involving premixed benzeneacetylene mixtures were carried out in a silica bulb (volume = 70 cm^3) connected to the mass spectrometer via a molecular leak.^{4,7} Acetylene (AGA) was bubbled through water to remove traces of acetone, condensed, and finally vacuum-distilled into a bulb. Styrene (Aldrich) and benzene (Erba) were used as received.

Results and Discussion

with

Rate Constant for the Addition of Acetylene to Benzene. Series of experiments were performed with (acetylene + benzene) mixtures in the ranges $0.11 < x_{HCCH} < 0.33$, $35 < P_{total} < 68$ Torr, 878 < T < 973 K. Typical HCCH decay profiles are shown in Figures 1 and 2. As found previously, reproducible results could be obtained only in conditioned reactors.^{4,7} No evidence of induction periods longer than about 10 s could be discerned in these experiments. Mass spectrometric analysis of reaction mixtures revealed products of masses 52 (C₄H₄), 104 (C₈H₈), and 128 (C₁₀H₈).⁴

These results were analyzed in terms of the mechanism

$$HCCH + C_6H_6 \rightarrow C_8H_8 \tag{-1}$$

$$\mathrm{HCCH} + \mathrm{HCCH} \to \mathrm{C}_4\mathrm{H}_4 \tag{2}$$

$$HCCH + C_4H_4 \rightarrow C_6H_6 \tag{3}$$

$$C_4H_4 + C_6H_6 \to C_{10}H_{10}$$
 (4)

$$\log k_{\rm e} = 10.5 - 9660 / T \tag{II}$$

$$\log k_3 = \log k_4 = 8.65 - 6580/T$$
(III)

in $M^{-1} s^{-1}$ units, which do not include stoichiometric coefficients. We adopted for k_2 the values recommended by Kiefer et al.¹⁶ and, for reaction 3, those of ref 17. The identity $k_3 = k_4$ is equivalent to assuming that vinylacetylene resembles acetylene: their association reactions are preceded by isomerization into the corresponding carbenes vinylidene (H₂C=C:) and vinylvinylidene (C₂H₃(H)C=C:), respectively. Since we observe species of mass



Figure 2. Open circles: decay of acetylene in mixtures: $[C_2H_2]_0 = 1.93 \times 10^{-4} \text{ M}$, $[C_6H_6]_0 = 3.99 \times 10^{-4} \text{ M}$, T = 948 K. Solid line calculated from a mechanism comprising reactions -1, 2, 3, and 4 (see text).



Figure 3. Solid squares: Arrhenius plot of k_{-1} values derived as described in the text. Solid line: $\log k_{-1}(M^{-1} s^{-1}) = 10.20 - 9000/T$.

128, rather than 130, the initial products of reaction 4 (viz. methylindene, dihydronaphthalene, etc.¹⁸ must undergo H₂ elimination under present conditions. Modeling HCCH decay was performed by means of an adapted version of CHEMKIN using k_{-1} as the only adjustable parameter. The results of these calculation are shown in Figures 1 and 2 (solid lines) and lead to the expression (see Figure 3)

$$\log k_{-1} (M^{-1} s^{-1}) = (10.20 \pm 0.76) - (9000 \pm 700) / T$$
 (IV)

which yields k_{-1} values comparable (about a factor of 2 larger) to k_2 in this temperature range, in agreement with previous reports⁴ and with the assumption that both reactions involve a common, very reactive intermediate. In Figures 4 and 5 we present values of $S_i(t)$, the sensitivity coefficient of acetylene concentration to the rate constant of step *i*:

$$S_i(t) = (\partial \ln [C_2 H_2]) / \partial \ln k_i$$
 (V)

It is apparent that reaction -1 clearly dominates the kinetics of acetylene decay in these mixtures, i.e., that the derived k_{-1} values are robust estimates. Since S_3 and S_4 are negligible at times shorter than 200 s, reactions 3 and 4 are merely included to account for the fate of vinylacetylene.



Figure 4. Sensitivity coefficient for acetylene S_i relative to reactions: (-1) solid squares, (2) solid circles, for the conditions of Figure 1. S_3 and S_4 (not shown) are negligible.





Remarkably, this mechanism is able to simulate observed profiles of acetylene decay in benzene/acetylene mixtures, at least in their initial stages, as a linear superposition of the known rates of the component reactions. The simplest rationalization of this event is that each step actually stands for an elementary bimolecular process.

Styrene Decomposition

Product Analysis. Above 1180 K the mass spectra of effusing gases resulting from styrene pyrolysis indicated the presence of a new ion at m/z = 26 (C₂H₂⁺). At the same time the signal at m/z = 78 (C₆H₆⁺, a fragment of C₈H₈⁺ itself) showed a gradual increase relative to the parent ion of the reactant at m/z = 104. In Figure 6 one can see that up to ca. 1180 K plots of ϕ_i vs $m_i^{1/2}$ are linear, as expected for a single neutral of mass 104 in the beam (eq I). By contrast, at 1300 K the phase shifts of masses 39, 52, and 78 align themselves but leave ϕ_{104} below and ϕ_{26} above the connecting line. This is taken as direct evidence that the products of styrene decomposition are indeed acetylene and benzene, the latter possessing a mass spectrum displaying fragments at m/z= 39 and 52 in addition to its molecular ion at m/z = 78. It should be emphasized that no radical species, such as phenyl of vinyl radicals, could be detected during styrene pyrolysis although we were able to find benzyl and methyl radicals as products of ethylbenzene decomposition under similar experimental conditions.14,15 These observation establish the non-radical nature of reaction 1.

Kinetic Data. Unimolecular rate constants $k_{1,uni}$ were evaluated from

$$k_{1,\text{uni}} = k_{e,104} f / (1 - f)$$
 (VI)

where $f = (I_0 - I)/I_0$; I and I_0 represent the intensities of the m/z= 104 signal at T and in the absence of decomposition, respec-



Figure 6. Phase shifts φ_i for the different fragment ions as function of $m_i^{1/2}$. Open circles: 1180 K. Open triangles: 1300 K; φ_{104} and φ_{26} deviate from the line connecting the ions at m/e = 78, 52, and 26, indicating that they belong to a heavier and lighter neutral, respectively.



Figure 7. Dashed line: Arrhenius plot for the high-pressure rate constant of reaction 1 given by eq VIII: $\log k_1 = 14.38 - 17076/T$. Solid circles: experimental values of $k_{1,uni}$. Solid line: extrapolated values from eq VIII to experimental conditions using the UNIMOL program (see text).

tively. We wish to point out that the same rate constants could be obtained from the signals corresponding to the acetylene molecular ion, now obtained at full (T > 1350 K) and partial styrene decomposition. We also verified that a tenfold variation in styrene flow rates did not modify either the product distribution or the rates. Experimental values of $k_{1,\text{uni}}$ are shown in Figure 7.

Evaluation of High-Pressure Arrhenius Parameters for Reaction 1. It is apparent that $k_{1,uni}$ values in Figure 7 do not fall on a straight line as would be expected for an elementary unimolecular reaction in its high pressure limit. Assuming that the Arrhenius parameters for the reverse reaction -1, equation II, correspond to the equilibrium energy distribution, one can calculate $k_1 = k_{1,\infty}$ using the overall equilibrium constant:¹⁰

$$\log (k_1/k_{-1}) = \log K_{1c} = 7.586 - \log T - 8458/T$$
(VII)

$$\log (k_1, s^{-1}) = 14.38 - 17076/T$$
(VIII)

at $\langle T \rangle = 928$ K. A RRKM extrapolation of eq VIII to the conditions of Figure 7 requires only additional information about β_{ω} , the gas-wall collision efficiency for internal energy transfer. We estimated β_{ω} values using the expression $\beta_{\omega} = 23.5 \exp(-4.11)$

× 10⁻³T), based on King and Gilbert's recipe, which involves the normal boiling temperature of styrene.¹⁹ Assignments of molecular parameters for styrene and the transition state of reaction 1 are given in the Appendix. We assumed negligible geometrical changes and adiabatic external rotations for this relatively tight complex. Calculations were performed using the UNIMOL package without conservation of angular momentum.²⁰ The solid curve in Figure 7 was evaluated in the strong collision approximation at the equivalent concentrations $[M]_{eq}$, defined by $\beta Z_{LJ}[M]_{eq} = \beta_{\omega}\omega$, since the nonrandom distribution of mean free paths in the low pressure reactor prevents application of master equation methodology to gas-wall internal energy exchange. Similar calculations for the experimental conditions of Figures 1 and 2 led to falloff factors of about 0.98, validating our initial assumption about the prevalence of a "high-pressure" regime.

The excellent fit obtained in Figure 7 confirms the soundness of this analysis and the hypothesis that the addition of acetylene to benzene is a truly bimolecular reaction. Rates of reaction 1, based on extrapolation of equation VIII to the conditions of recent shock-wave studies with $\beta_c = 0.01$ (M = argon), are about a factor 1.4 larger at 1700 K and a factor of 3.6 larger at 2200 K than reported data. By contrast, extrapolation of shock tube results to the experimental conditions of Figures 1 and 2 leads to gross disagreements: predicted rates are faster by a factor of 60 at 870 K and by a factor of 18 at 970 K. These observations suggest that shock tube rates, although perhaps somewhat slow, are more reliable than the derived Arrhenius parameters. In any case, present kinetic data for the pyrolysis of styrene, which are based on measurements for the direct and reverse processes, should be preferred.

Mechanism of Reaction 1. In Figure 8 we present an energy diagram including species of interest (see the Appendix II). It is apparent that the high-pressure activation energy of reaction 1 obtained in this work allows for the generation of vinylidene as a primary fragment. This is in accord with our previous conclusions based on the relative rates of reactions -1 and 24 and on the mechanism of vinylacetylene unimolecular decomposition.^{6,16} Since vinylidene is expected to add indiscriminately to π -double bonds with negligible (i.e., $\approx 2 \text{ kcal/mol}$) activation energies, the transition states for the extrusion of vinylidene from other C_8H_8 hydrocarbons are predicted to lie at or above (112) \pm 2) kcal/mol.⁷ In this context it is hardly coincidental that barrelene, a 38 kcal/mol less stable isomer of styrene, also fits into this scheme.¹¹ On this basis we suggest that both styrene and barrelene decompositions proceed by concerted equilibration with 7-methylene bicyclic intermediates, [4.1.0]-7-methylene cycloheptadiene and [2.2.1]-7-methylene cycloheptadiene, respectively, followed by the rate-determining elimination of vinylidene:



It is remarkable that their pathways are not interconnected below the exit transition states as revealed by the fact that styrene is absent among the products of barrelene decomposition. It can be shown that the [4.1.0] intermediate implicated in the decomposition of styrene can account as well as its [4.2.0] isomer for the isotope labeling experiments of ref 3. Notice that although the direct elimination of acetylene from barrelene is conceivable,¹¹ the same process in styrene or vinylacetylene would require a simultaneous [1,3] H shift. We consider very unlikely for the transition states of such diverse reactions to have similar A factors and energies just lying on the thermochemical threshold for the generation of vinylidene! The thermal decomposition of 1,3,5,7 cyclooctatetraene, whose summit lies 13 kcal/mol above this threshold, is not inconsistent with the extrusion of vinylidene after crossing a high-energy ridge probably associated with ring contraction.12,21



Figure 8. Energy diagram for the species of interest. Open bar indicates the equipotential line at $[\Delta H_f(\text{vinylidene}) + \Delta H_f(\text{benzene})] = 112$ kcal/mol. COT = cyclooctatetraene. See Appendix II for additional information.

	Г	ABLE	I:	Therm	ochemical	Data	(298	K)	1	1
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	$\Delta H_{\rm f}^{\circ}$	S°	
compound	(kcal/mol)	(cal/mol K)	ref
styrene	35.2	82.5	9
acetylene	52.4	48.1	9
benzene	19.8	64.5	9
$({}^{1}A_{1})$ vinylidene	92.4	53.4	7, 22
barrelene	73.0	82.7	9, 11
cyclooctatetraene	71.0	78.2	9
[4,1,0]-7-MHD ^b	90.7	82.5	
[2,2,1]-7-MHD ^b	78.0	84.9	9
5-vinyl-1,3-cyclo-hexadiene	43.8	87.4	9
5-vinyl-1,4-cyclo-hexadiene	43.5	91.0	9
biradical $(BR)^b$	127.4		

^a Figures in italics are estimates (see Appendix I). ^bSee Appendix I for explanation.

We have already presented several arguments rejecting a biradical path for the dimerization of acetylene and its reverse process, the decomposition of vinylacetylene.⁷ It can be shown that a biradical mechanism for reactions (1,-1) is impossible. We estimate (see Appendix II) for the heat of formation of the putative biradical intermediate



 $\Delta H_{\rm f}(BR) = 127.4$ kcal/mol, and therefore that $E_{-1} = 53.5$ kcal/mol, i.e., about 12 kcal/mol larger than the experimental value of 41.2 kcal/mol from eq IV.

Summing up: styrene decomposes into acetylene and benzene in one step. We prove that this process that does not involve free monoradicals or biradicals. We argue that the similar energies of the transition states (112 kcal/mol), that correspond to widely different activation energies for styrene (78 kcal/mol) and barrelene (42 kcal/mol) pyrolyses, represent strong evidence against concerted pathways connecting closed-shell species but favor the formation of nascent vinylidene. Since the lifetime of $({}^{1}A_{1})$ $H_2C==C$: is only a few picoseconds, the standard proofs of existence, namely, its generation from a suitable precursor followed by trapping, or its direct detection as a product of the reverse process, appear hardly viable. If vinylidene, rather than acetylene, were the leaving species in this type of reactions one could estimate the rate of acetylene addition to, or elimination from, π -bonds within a factor of 2, solely based on the thermochemistry of reactants and products.

Acknowledgment. This work was financially supported by CONICET of Argentina. Mr. O. Lopez carried out some of the pyrolytic experiments.

Appendix I

Input Data for RRKM Calculations. Ground-state frequencies $[cm^{-1}]$: 3100, 3050 (5), 3020, 2990, 1620, 1600 (2), 1500 (1),

1450 (2), 1340, 1320, 1280, 1220, 1160 (2), 1050 (2), 1020, 1000 (3), 960, 950 (2), 900, 840, 830, 800 (3), 750, 600, 500, 410, 300 (2).

Transition-state frequencies $[cm^{-1}]$: 3100, 3050 (5), 3020, 1620, 1600 (2), 1500 (1), 1450 (2), 1340, 1320, 1280, 1160 (2), 1020, 1000 (3), 900, 840 (2), 800 (3), 780 (2), 750, 744, 743, 700 (3), 500 (2), 260 (2).

Ratio of overall moments of inertia $(I^+/I) = 1$.

Critical energy = 75.00 kcal/mol; collision frequencies calculated as $(\beta_{\omega}\omega)$ (see text).

Appendix II

Thermochemical Data are given in Table I.

Thermochemical Estimates (298 K).²³ Barrelene (bicyclo-[2.2.2]octa-2,5,7-triene). Entropy: Open-chain starting compound: 3 vinyl-1,4-cyclohexadiene. $S^{\circ}_{int} = 91.0 \text{ cal/mol K}$; entropy decrement in closing a C6 ring $\Delta S^{\circ}_{int rot} = -4.7 \text{ cal/mol K}$; symmetry corrections ($\sigma = 6$) $\Delta S^{\circ}_{\sigma} = -3.6 \text{ cal/mol K}$; thus $S^{\circ} = 82.7 \text{ cal/mol K}$.

[4.1.0]-7-MHD (7-methylenebicyclo[4.1.0]hepta-2,4-diene). Entropy: Open-chain starting compound 5 vinyl 1,3 cyclohexadiene. $S^{\circ}_{int} = 87.4$ cal/mol K. Entropy decrement in closing the C3 ring $\Delta S^{\circ}_{int rot} = -4.9$ cal/mol K. Thus, $S^{\circ} = 82.5$ cal/mol K. Heat of formation:

 $\Delta H^{\circ}_{f} = \Delta H^{\circ}_{f} [Cd-(H)_{2}] + \Delta H^{\circ}_{f} [Cd-(C)_{2}] + 2 \Delta H^{\circ}_{f} [C-(Cd)_{2}] + \Delta H^{\circ}_{f} [Cd-(H)(C)] + 2\Delta H^{\circ}_{f} [Cd-(H)(Cd)] + \Delta H^{\circ}_{RC} (methylene cyclopropane) + \Delta H^{\circ}_{RC} (1,3-CHD)$

$$\Delta H^{\circ}_{f} = 6.76 + 10.34 + 2(-1.48) + 2(6.78) + 2(8.59) + 41 + 4.8 = 90.7 \text{ kcal/mol}$$

[2.2.1]-7-MHD (7-methylenebicyclo[2.2.1]hepta-2,5-diene). Entropy: Open-chain starting compound 3 vinyl 1,4 cyclohexadiene. $S^{\circ}_{int} = 91.0 \text{ cal/mol K}$. Entropy decrement in closing a tight C5 ring $\Delta S^{\circ}_{int rot} = -4.7 \text{ cal/mol K}$. Symmetry corrections ($\sigma = 2$) $\Delta S^{\circ}_{\sigma} = -1.4 \text{ cal/mol K}$. Thus $S^{\circ} = 84.9 \text{ cal/mol K}$. Biradical BR (5-vinyl (2'-yl) 1,3-c-hexadien-6-yl):

 $\Delta H^{\circ}_{f}(BR) = BDE[C_{2}H_{3} - H] + BDE[(1,3-CHD-5-yl) -$

H] - BDE[H - H] + ΔH°_{f} [5-vinyl-1,3-cyclohexadiene] = 111.2 + 76.2 (ref 24) - 104 (ref 25) + 44.2 =

127.4 kcal/mol

Registry No. C₆H₅CH=CH₂, 100-42-5; C₆H₆, 71-43-2; HC=CH, 74-86-2.

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Dynamics of the $O(^{1}D)$ + CINCO Reaction

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The reaction of excited O(¹D) atoms with ClNCO was studied by pulsed photolysis of O₃/ClNCO mixtures with the 249-nm output of a KrF laser. The rate constant for O(¹D) quenching by ClNCO was determined to be $k = (1.3 \pm 0.3) \times 10^{-10}$ cm³ s⁻¹. Investigation of the possible products of this reaction indicated that production of ClO + NCO is a major channel, with a branching fraction greater than 0.20. No evidence was found for the production of NCl in its $X^3\Sigma$ -, $a^1\Delta$, or $b^1\Sigma^+$ states. An upper limit for the branching fraction to NCl + CO₂ is 0.005.

Introduction

In previous issues of this journal, we have presented results from studies of the dynamics of reactions of excited $O(^1D)$ atoms with HN₃ and HNCO.¹⁻³ These processes are of interest in view of the similarity of $O(^1D)$ to isoelectronic NH($a^1\Delta$), a species whose reactions with HN₃ and HNCO are known from studies of the photochemistry of these molecules.^{4,5} $O(^1D)$ appears to behave much like NH(a) in its reaction with HN₃; chemiluminescence from the system is indicative of formation of OH and N₃ in the initial step. The $O(^1D)$ + HNCO reaction is very different, however, in that the dominant path is electrophilic attack by the excited oxygen atoms on the NCO chain, generating NH and CO₂. Although much of the energy released by this reaction comes from formation of the new C-O bond (a major difference from the $O(^1D)$ + HN₃ reaction), angular momentum constraints force the system to produce NH in its excited $a^1\Delta$ state. Indeed, production of NH(a) + CO₂ is the dominant path for the reaction, a remarkable result given the complexity (and presumed lack of