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Kinetics of Pyrolysis of a Coal Model Compound, 2-Picoline, the Nitrogen Heteroaromatic Analogue of Toluene. 2. The 2-Picolyl Radical and Kinetic Modeling

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The pyrolysis of 2-picoline, investigated experimentally in our previous paper,[1] has been successfully modeled using a 70-reaction free-radical mechanism. The mechanism includes decomposition pathways for *o*-pyridyl and 2-picolyl, both of which are formed through the principal initiation reactions of 2-picoline. The proposed mechanism for 2-picolyl decomposition involves the direct ring opening of the 2-picolyl radical. Further reactions of the open chain isomer of 2-picolyl resulted in the formation of the major products HCN and acetylene and the minor products 1-cyanocyclopentadiene and cyclopentadiene. Kinetic modeling confirmed the feasibility of this mechanism by predicting the observed profiles for these species. Optimizing of the heat of formation of 2-picolyl through kinetic modeling resulted in a value of 68 (±5) kcal mol^{-1}. This value suggests a lower level of resonance stabilization for 2-picolyl compared to benzyl. This inference is supported by the "normal" value of the rate constant for 2-picolyl + H recombination found by modeling to be in the range 1×10^{13}–6×10^{13} cm^3 mol^{-1} s^{-1}. The reactant and product profiles predicted by the kinetic model were found to be very sensitive to the rate of the initiation reaction yielding methyl and *o*-pyridyl radicals, allowing the heat of formation of the *o*-pyridyl radical to be determined. The optimized rate constant for this initiation reaction was found to be $10^{16.1(\pm 0.2)}$ exp(−91.5 (±2) kcal mol^{-1}/RT) s^{-1}, corresponding to a heat of formation for the *o*-pyridyl radical of 84.1 (±2) kcal mol^{-1}.

Introduction

The thermal decomposition of toluene, whose nitrogen heteroaromatic analogue 2-picoline might be considered to be, has been much studied under conditions relating to combustion and sooting. Despite over a decade of studies generally using shock tubes, there are several unresolved problems concerning the kinetics of pyrolysis of toluene and the mechanism of thermal decomposition of the intermediate radical, benzyl.[2-7]

In part, these problems arose from uncertainties in the relative dominance of the initiation reactions of toluene (C_7H_8)

$$C_7H_8 \rightarrow C_7H_7 + H \qquad (a)$$

forming benzyl radicals and

$$C_7H_8 \rightarrow C_6H_5 + CH_3 \qquad (b)$$

producing phenyl and methyl radicals.[2,4,6] The situation has been further confused until recently by a lack of knowledge of the thermochemistry of the benzyl radical and by the unexpectedly rapid rate of recombination of benzyl and H atoms[8] (reaction −a). Furthermore, a detailed understanding of toluene decomposition kinetics awaits resolution of the uncertainties in the mechanism of decomposition of the benzyl radical. As yet, only the stoichiometry of the production of H atoms from benzyl

$$C_7H_7 \rightarrow \text{benzyl fragments} + H \qquad (c)$$

can be said to be known with any certainty although benzyl fragments have been variously claimed to include C_3H_3, C_5H_5, C_2H_2, and C_4H_4 species.

Low-rank coals often contain significant amounts of fuel-bound nitrogen (FBN) present in both substituted and condensed five- and six-membered rings. 2-Picoline is a useful model compound for a study of the evolution of FBN to volatile precursors of NO_x in the fuel-rich combustion of low-rank coals, and in a previous kinetic study we have reported overall kinetics of pyrolysis of 2-picoline, identified products of the decomposition, and used UV spectroscopy to investigate reaction intermediates in the region 290–360 nm. By analogy with toluene pyrolysis, we would expect the 2-picolyl radical to be an important intermediate in the pyrolysis or fuel-rich combustion of 2-picoline or fuels containing this moiety. There have been no previous kinetic or thermochemical studies of picolyl radicals, so that a study of the thermal reactions of these radicals should not only yield information of importance in understanding NO_x formation from FBN but should also provide fundamental information about the extent of resonance stabilization in a nitrogen heteroaromatic free radical. In addition, the presence of the ring nitrogen in picolyl radicals might serve as a chemical marker in the decomposition products hence possibly assisting in the unravelling of similar reaction pathways in the decomposition of benzyl radicals.

In the present work, therefore, we have chosen to study by kinetic modeling the rate of decomposition and the products obtained from the thermal decomposition of 2-picolyl radicals

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produced by pyrolysis of 2-picoline vapor dilute in argon in a single-pulse shock tube.

Results and Discussion

Products. The previous observation that a major initial nitrogen-containing product is 1-cyanocyclopentadiene with $m/z = 91$, i.e., 1 amu less than that of the 2-picolyl radical, is important and implies that we are observing the initiation reaction of 2-picoline ($C_5H_4NCH_3$):

$$C_5H_4NCH_3 \rightarrow C_5H_4NCH_2 + H \quad (1)$$

followed by

$$C_5H_4NCH_2 \rightarrow [C_6H_5N]_{m/z=91} + H \quad (8, 11, 12)$$

where the reaction numbering follows the reaction mechanism given in Table I. The $m/z = 91$ species in parentheses is meant to signify more than one such species leading to the observed 1-cyanocyclopentadiene. The early production of methane would be expected to arise from the alternative initiation of 2-picoline:

$$C_5H_4NCH_3 \rightarrow C_5H_4N + CH_3 \quad (2)$$

where the methyl radicals so produced give rise to the observed methane by subsequent abstraction reactions.

The presence of pyridine at very low extents of decomposition could arise either by the *o*-pyridyl radical produced in (2) recombining with H atoms, or pyridine could be formed directly through displacement of methyl radicals in 2-picoline by H atoms:

$$C_5H_4NCH_3 + H \rightarrow C_5H_5N + CH_3 \quad (29)$$

The analogous displacement of methyl by H atoms in toluene, yielding benzene, is known to occur.[9-11]

Thermochemical Considerations. The interpretation of the reaction pathways involving 2-picolyl radicals is assisted by a consideration of the thermochemistry of the picoline/picolyl system. We assume from an analysis of the low-temperature products of pyrolysis of 2-picoline that 2-picolyl radicals are principally formed in the initiation reaction 1 and also by the abstraction reactions

$$CH_3, H + C_5H_4NCH_3 \rightarrow C_5H_4NCH_2 + CH_4, H_2 \quad (3, 4)$$

involving H and CH_3 radicals produced by reactions 1 and 2. Let us now consider possible pathways for the disappearance of picolyl radicals. Although no thermochemical data exist for the 2-picolyl radical, we can make an estimate of its heat of formation by assuming that the difference in heats of formation of 2-picoline and 2-picolyl is the same as between toluene and benzyl. Hence we obtain $\Delta H°_{f,300}$(2-picolyl) $\approx$ 62 kcal mol^{-1}.

This study is the first to attempt to explain the decomposition pathway of 2-picolyl. The previous investigations of the decomposition of the analogous benzyl radical could be expected to be relevant here. Unfortunately however, the mechanism of benzyl decomposition is still poorly understood.

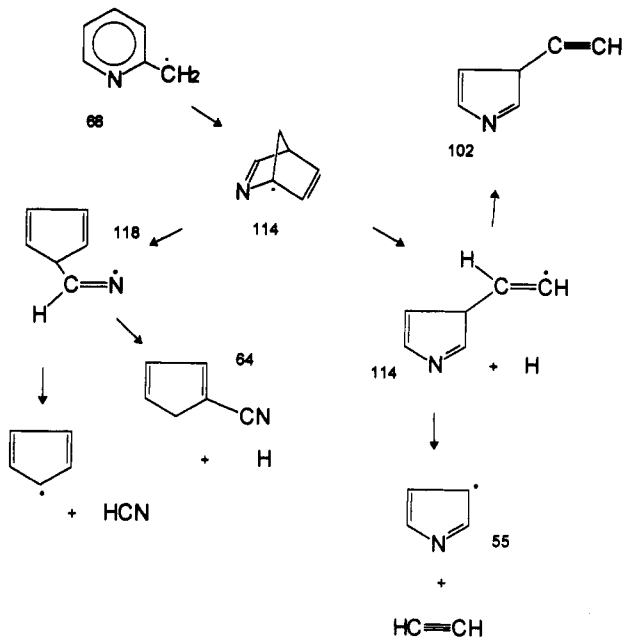
It has recently been proposed that benzyl could decompose via a norbornadienyl radical[6,12] intermediate. Braun-Unkoff et al.[6] proposed this pathway to account for the activation energy of 44.7 kcal mol^{-1} reported[13] for the reaction

$$C_7H_7(\text{benzyl}) \rightarrow C_5H_5(\text{cyclopentadienyl}) + C_2H_2$$

Braun-Unkoff et al. showed the above reaction must pass from benzyl to acetylene and cyclopentadienyl without initially forming a linear C_5H_5 radical. Any process involving a linear C_5H_5 radical would result in an activation energy much larger than 44.7 kcal mol^{-1}. By passing from benzyl, to norbornadienyl and then to products, it was claimed that cyclopentadienyl and acetylene could be produced with an activation energy consistent with the reported value of 44.7 kcal mol^{-1}.

It is interesting therefore to investigate the possibility that a N-containing analogue of norbornadienyl could be an important low-energy intermediate in the decomposition of 2-picolyl. The analogous products in the case of 2-picolyl would be either HCN and cyclopentadienyl or acetylene and pyrrolyl. The formation of HCN from 2-picolyl is consistent with our previous proposal[1]

SCHEME I: Reaction Scheme for Decomposition of 2-Picolyl Radical Passing through a Bicyclic Norbornadienyl Type Intermediate. Heats of Formation (kcal mol^{-1}) at 300 K Are Indicated



that HCN produced from the decomposition of 2-picoline results largely from the decomposition of 2-picolyl. The formation of cyclopentadiene as a reaction product in our study[1] also supports a norbornadienyl type intermediate, as this could easily be produced by recombination of H atoms with cyclopentadienyl.

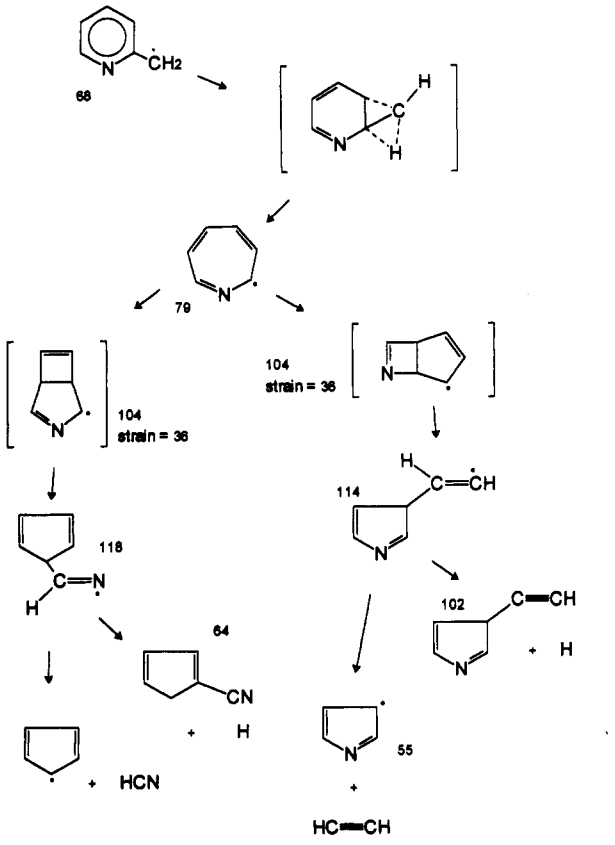
While the decomposition of 2-picolyl to HCN and cyclopentadienyl involving the N analogue of norbornadienyl appears to be feasible, acetylene and pyrrolyl should also form from this same intermediate. Recombination of pyrrolyl radicals with H atoms would then produce pyrrole. Neither pyrrole nor its decomposition products could be detected in the products of 2-picoline pyrolysis.[1] Unless the rate of formation of HCN and acetylene is greatly favored over the generation of acetylene and pyrrolyl, it seems unlikely that the N analogue of norbornadienyl plays a significant role in the decomposition of 2-picolyl.

If the presence of a norbornadienyl type intermediate is assumed, the absence of kinetic data for any of the reaction steps involving the decomposition of 2-picolyl means that thermochemical estimates must be used to determine the relative rate of HCN and cyclopentadienyl formation, compared to acetylene and pyrrolyl formation. Scheme I illustrates the pathways which are feasible involving a norbornadienyl type intermediate. Also included in the Scheme I are group additivity estimates for heats of formation at 300 K for the species involved. The thermochemistry of N-containing cyclic and bicyclic structures included in Scheme I are difficult to estimate due to the absence of data on the ring strain present for these compounds. The estimates of the ring strain are therefore made with analogy to hydrocarbon structures. Where applicable, the values for the ring strain used in the calculation of thermochemistry are included in the scheme.

Interpretation of the thermochemistry of Scheme I shows that the activation energy for the formation of HCN and cyclopentadienyl from 2-picolyl would be expected to be similar to that for production of acetylene and pyrrolyl. This suggests that Scheme I represents an unlikely mechanism for 2-picolyl decomposition. The minor products predicted also do not agree with the experimental observations. Although 1-cyanocyclopentadiene is predicted and observed experimentally,[1] substituted pyrroles are also predicted but are not observed experimentally.

The thermochemistry of Scheme I suggests an activation energy for the decomposition of 2-picolyl to HCN and cyclopentadienyl of approximately 60 kcal mol^{-1}. This value assumes 10 kcal mol^{-1} is required to form the norbornadienyl intermediate from 2-picolyl, in addition to the 50 kcal mol^{-1} endotherm for the reaction. Kinetic

SCHEME II: Reaction Scheme for Decomposition of 2-Picolyl Radical Passing through a Seven-Membered Ring Intermediate. Heats of Formation (kcal mol^{-1}) at 300 K Are Indicated



modeling indicated that this value was too low, as it proved to be impossible to model HCN formation at both low and high extents of decomposition using this value, where the Arrhenius preexponential factor was chosen to best fit the data. The decomposition of 2-picolyl to HCN and cyclopentadienyl via a norbornadienyl type intermediate therefore appears to be unlikely, considering both the minor pathways possible with this route and the kinetics of formation of HCN.

The presence of 1-cyanocyclopentadiene in the reaction products suggests other possible mechanisms for 2-picolyl decomposition. In the decomposition of phenylnitrene (C_6H_5N:), 1-cyanocyclopentadiene was observed as a major product.[14] The mechanism for phenylnitrene decomposition generally agreed upon involves the formation of a seven-membered ring,[15,16] followed by rearrangement to 1-cyanocyclopentadiene. The formation of 1-cyanocyclopentadiene from a seven-membered ring intermediate analogous to the cycloheptatrienyl radical could also be applied to the decomposition of 2-picolyl.

Thermochemistry is again useful in judging the feasibility of such a reaction pathway. An important species in this mechanism of 2-picolyl decomposition is the resonance-stabilized seven-membered ring. The heat of formation of this species was calculated using a resonance stabilization energy of 10 kcal mol^{-1}, slightly less than that determined for the cycloheptatrienyl radical.[17,18]

Pathways for 2-picolyl decomposition involving the seven-membered ring intermediate are detailed in Scheme II together with estimates of the heats of formation of the species involved. The scheme shows that HCN and cyclopentadienyl would be expected to be major products, with a minor pathway resulting in the formation of 1-cyanocyclopentadiene. The scheme also details other possible minor pathways of 2-picolyl decomposition.

It is interesting to compare Scheme I involving the norbornadienyl type intermediate with Scheme II. It can be seen that the immediate precursors to the products are the same in each case, suggesting that the two mechanisms might be kinetically very similar. The similarities also mean that the arguments advanced against Scheme I can also be applied to Scheme II. If 2-picolyl decomposed via Scheme II, one would expect to observe both pyrrole and substituted pyrroles, in the reaction products. The resonance stabilized seven-membered ring intermediate therefore appears unlikely for the same reasons as the norbornadienyl-type intermediate.

The decomposition of 2-picolyl does not appear therefore to involve rearrangement to a resonance-stabilized seven-membered cyclic radical. The phenylnitrene mechanism might therefore be relevant only to the reaction of carbenes or nitrenes and might not be appropriate for ring-expansion reactions of radicals. Loss of an H atom from the 2-picolyl radical would result in the formation of 2-pyridylcarbene, which is known to rearrange to 1-cyanocyclopentadiene by passing through phenylnitrene.[16] It might be possible that this represents a minor pathway in the decomposition of 2-picolyl, accounting for the formation of 1-cyanocyclopentadiene. The observation of traces of picolines in the products of phenylnitrene decomposition supports this possibility.[16]

The rearrangement of 2-pyridylcarbene to 1-cyanocyclopentadiene is reported to proceed rapidly,[16] meaning that in the case of 2-picolyl rearrangement, the loss of a H atom from 2-picolyl to form the carbene would be expected to be rate determining. The activation energy for this H fission could be estimated from the endotherm of the reaction. Wentrup[15] estimated the heat of formation of 2-pyridylcarbene to be 114 kcal mol^{-1}. This suggests 100 kcal mol^{-1} additional energy would be required to allow H fission from 2-picolyl to produce 2-pyridylcarbene.

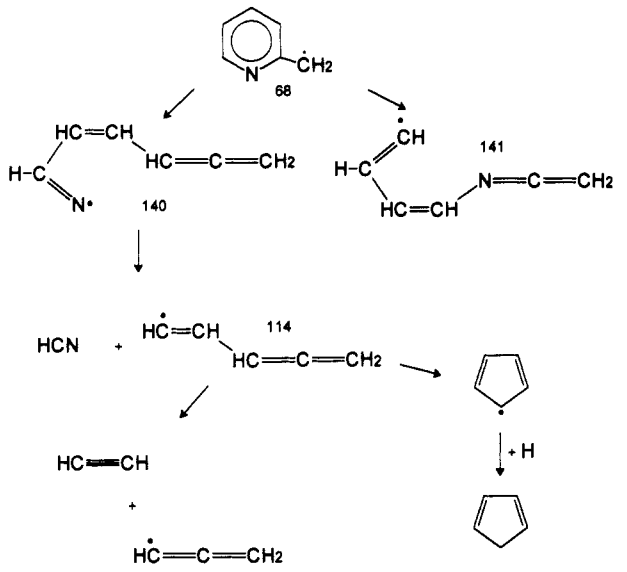
An activation energy of 100 kcal mol^{-1} for the formation of pyridylcarbene from 2-picolyl would prevent this carbene from being an intermediate in any major pathway of 2-picolyl decomposition. An activation energy of 100 kcal mol^{-1} was also shown by kinetic modeling to greatly underpredict the experimentally observed[1] concentrations of 1-cyanocyclopentadiene. We cannot assert, however, that 1-cyanocyclopentadiene is not being formed from 2-picolyl via 2-pyridylcarbene. It can only be concluded that it is unlikely to be an important route for formation of 1-cyanocyclopentadiene.

The possibility that 2-picolyl may decompose via direct ring opening might seem unlikely on the basis of the high activation energy required for such a process. In the case of the *o*-pyridyl radical, the pyridyl ring opens directly to a relatively stable cyano radical.[19] In contrast to the *o*-pyridyl case, there is no direct means of opening the 2-picolyl to a cyano radical. The least unlikely products of direct ring opening involve the formation of either an iminyl radical ($H_2C{=}C{=}CH{-}CH{=}CH{-}CH{=}N^{\bullet}$) or an imine containing a vinyllic radical ($H_2C{=}C{=}N{-}CH{=}CH{-}CH{=}CH^{\bullet}$). These possibilities arise from ring opening in the 1–2 and the 2–3 positions respectively. Scheme III illustrates these reactions. Other possible ring-opening pathways would result in biradical formation and would therefore be a minimum of 20 kcal mol^{-1} more endothermic than the most likely possibilities detailed in Scheme III.

Included as part of Scheme III are thermochemical estimates of the radicals formed from the ring opening of 2-picolyl. The estimates were made using Benson's rules of group additivity.[20] It should also be noted that the radical sites in either of the two radicals would not be expected to be delocalized significantly, thereby reducing one of the major sources of error often associated with group additivity estimates. The thermochemistry of the open-chain radicals suggests that the two pathways would be endothermic by approximately the same amount, requiring approximately an additional 80 kcal mol^{-1} from 2-picolyl or 120 kcal mol^{-1} from 2-picoline.[21]

As concluded previously,[1] the experimental results suggest that 2-picolyl probably decomposes to form HCN and other products. Since HCN appears to stem mainly from the 2-picolyl route, a pseudo-Arrhenius plot for the formation of HCN may give an apparent activation energy for decomposition via 2-picolyl. The pseudo activation energy for HCN formation[1] is 110 (±10) kcal mol^{-1}. However, Arrhenius parameters for formation obtained from a complex mechanism should be interpreted with caution,

SCHEME III: Direct Ring-Opening Mechanism for the Decomposition of 2-Picolyl Radicals Leading to the Formation of HCN and Cyclopentadiene. Heats of Formation (kcal mol^{-1}) at 300 K Are Indicated



and the error in the apparent activation energy of formation is considerable. Nonetheless, the result shows that although the activation energy for ring opening is relatively high, it is not inconsistent with the experimental data.

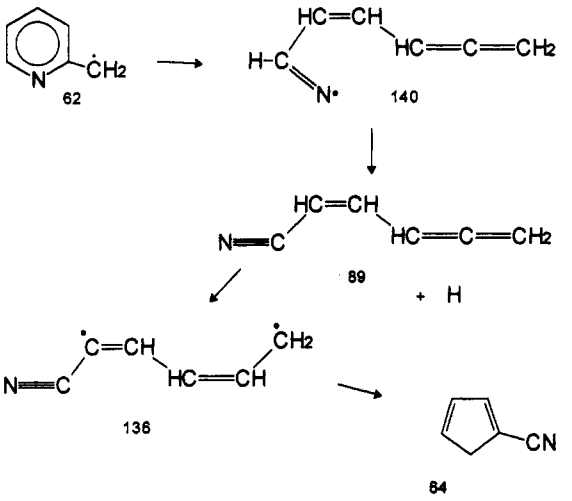
The above argument suggests that direct ring opening is a possible pathway for the decomposition of 2-picolyl. Ring closing of either of the open-chain radicals, however, would be very fast. Although recyclization would be expected to possess a low Arrhenius preexponential factor, it could proceed with an activation energy barrier as low as 5 kcal mol^{-1}. Any route leading to products from the open-chain radical must be facile in order to compete with ring closure and hence form products.

Of the two possible open-chain radicals formed from 2-picolyl (Scheme III), only the iminyl radical could undergo near thermoneutral fission. Scheme III illustrates the formation of HCN and an open-chain C_5H_5 radical from the iminyl radical and possible subsequent reactions of the open chain C_5H_5 radical. Where thermochemical data are not available, the heats of formation included in the scheme have been obtained by group additivity. The linear C_5H_5 radical could undergo further fission to yield acetylene and propargyl. Acetylene was observed as a major product of the decomposition of 2-picoline, and the most likely fate of propargyl would be the formation of benzene, which is also observed in the reaction products.[1]

An alternative fate of the linear C_5H_5 radical would be cyclization. The radical so formed could then rapidly rearrange to the resonance stabilized cyclopentadienyl radical. The observed product, 1,3-cyclopentadiene, would be expected to arise from recombination of cyclopentadienyl with H atoms. Traces of 1- and 2-methyl-1,3-cyclopentadiene detected in the reaction products in approximately equal amounts are also consistent with the presence of the cyclopentadienyl radical.

The experimentally observed products appear to be consistent with the decomposition of the linear iminyl radical by the route proposed in Scheme III. There would appear to be an anomaly with this mechanism for 2-picolyl decomposition, however. It might be expected that the loss of an H atom from the open-chain iminyl radical could compete with fission into HCN. Loss of the H atom might be expected to result in the formation of a stable open-chain nitrile, of mass 91. The heat of formation of this species (cyanovinylallene, $H_2C{=}C{=}CH{-}CH{=}CH{-}CN$) can be calculated from group additivity to be approximately 89 kcal mol^{-1}, making its formation from the open-chain iminyl radical close to thermoneutral. This might be expected to result in similar behavior to that observed for the ring opening of *o*-pyridyl, where five stable nitriles of mass 77 (isomers of cyanovinylacetylene)

SCHEME IV: Direct Ring-Opening Mechanism for the Decomposition of 2-Picolyl Radicals Leading to the Formation 1-Cyanocyclopentadiene. Heats of Formation (kcal mol^{-1}) at 300 K Are Indicated



are formed via loss of an H atom after ring cleavage, followed by the rearrangement of the open chain nitrile. The loss of an H atom from 2-picolyl after ring opening might therefore be expected to result in a number of straight-chain nitriles of mass 91, from the isomerization of cyanovinylallene. No open chain nitriles of mass 91 were observed in the pyrolysis of 2-picoline,[1] with 1-cyanocyclopentadiene being the only nitrile of mass 91 detected.[1]

This apparent anomaly can be explained if cyanovinylallene is able to rearrange readily to 1-cyanocyclopentadiene. Unsaturated nitriles are known to undergo facile unimolecular rearrangement to form isomeric nitriles over the temperature range studied here.[22,23] In a previous study of isomerization and pyrolysis of the butenenitriles,[24] allyl cyanide and *cis*- and *trans*-crotononitrile were found to interconvert rapidly at approximately 1300 K. Relevant to the present study was the detection of traces of cyclopropyl cyanide arising from the rearrangement of allyl cyanide and crotononitrile.[24]

Apparent differences in the behavior of open-chain nitriles of mass 91 when compared to other previously studied unsaturated nitriles could be a consequence of the low heat of formation of 1-cyanocyclopentadiene. From group addivity the heat of formation of 1-cyanocyclopentadiene is ≈64 kcal mol^{-1}. This is approximately 25 kcal mol^{-1} lower than the heat of formation of cyanovinylallene. A possible route for the formation of 1-cyanocyclopentadiene from cyanovinylallene is outlined in Scheme IV. The activation energy for the rearrangement would be close to the energy needed to form the biradical intermediate (Scheme IV).[20] This would result in an activation energy of approximately 50 kcal mol^{-1}. A unimolecular reaction with an activation energy of 50 kcal mol^{-1} might be expected to proceed quite rapidly over the temperature range of the present study. Since the activation energy of the reverse reaction, i.e., ring opening, should be ≈25 kcal mol^{-1} higher than for the ring-closing reaction, it is most likely that open-chain nitriles of mass 91 would only be present in very small concentrations. Kinetic modeling (see below) confirms this postulate.

The decomposition of 2-picolyl by ring-opening explains how the major products HCN and acetylene, and the minor products 1-cyanocyclopentadiene, 1,3-cyclopentadiene, and benzene are formed. Mechanisms for the formation of the minor products acetonitrile, cyanovinylacetylene, and acrylonitrile have not yet been proposed. Although these products were observed in the pyrolysis of pyridine,[19] suggesting their formation from *o*-pyridyl, kinetic modeling assuming their formation from *o*-pyridyl alone resulted in the model underpredicting the yields of these species by at least a factor of 5. It is therefore possible that there may be an additional mechanism for the formation of acetonitrile, cyanovinylacetylene, and acrylonitrile.

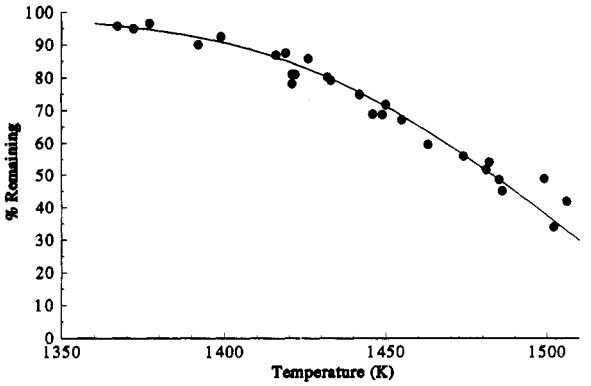


Figure 1. Comparison of the experimental percent 2-picoline remaining (points) with the predictions of the reaction model of Table I (line).

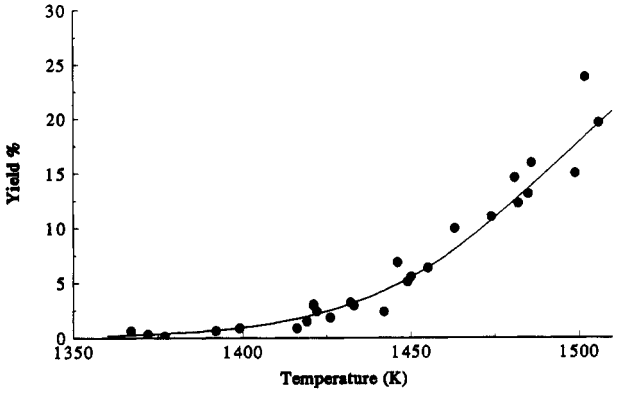


Figure 2. Comparison between the experimental yield (scaled by the initial reactant 2-picoline) of hydrogen cyanide (points) and the predictions of the reaction model of Table I (line).

The discussion of the decomposition of the parent 2-picoline has thus far only considered the possibility of H abstraction from the methyl group. This approach is justified if only the major pathways are to be considered, as abstraction from the side chain of 2-picoline would be expected to be considerably faster than abstraction from any of the ring positions if we may use the toluene analogy.[9]

Although the above argument implies major products could not be derived from routes involving the abstraction of ring hydrogens of 2-picoline, the formation and decomposition of 2-methylpyridyl radicals could explain minor products observed. Hydrogen abstraction from the 2, 4, and 5 positions of 2-picoline yields 2-methylpyridyls, which could undergo further reaction to give observed products. Scheme V illustrates the reactions of the 2-methylpyridyls and includes thermochemical estimates of the species involved and species names used in the kinetic model (Table I). The relatively low barriers to these reactions of the 2-methylpyridyls imply that the abstraction rate of the ring hydrogen is rate determining. Minor products would therefore be expected to form from these routes as the abstraction of picollylic hydrogens would be much faster than ring abstraction to yield 2-methylpyridyls.

Kinetic Modeling. A detailed model for the decomposition of 2-picoline has been developed and is included in Table I. The structures and thermochemical parameters of selected species appearing in the mechanism are included in Table II.

Kinetic modeling was carried out using the Sandia CHEMKIN code,[25] together with a shock tube code[26] which has been modified to account for conditions during the cooling wave, and the ordinary differential equation solver, LSODE.[27] Rate of production and sensitivity analysis were carried out using the SENKIN[28] code.

Predicted decomposition and product profiles from the mechanism in Table I are compared with experimental data for the reactant and major products in Figures 1–6. For the minor products cyanovinylacetylene, acrylonitrile, and acetonitrile, model predictions fall within the scatter of the experimental data. Ethane

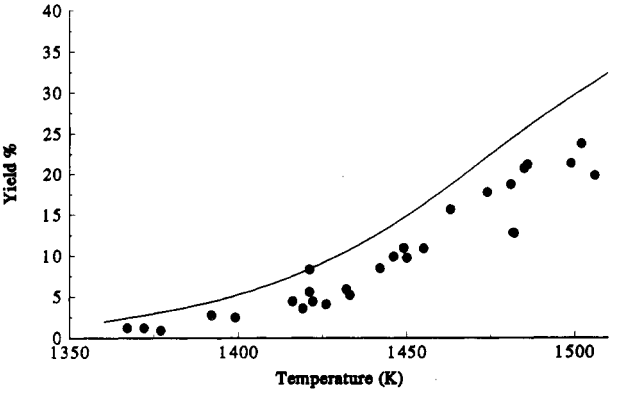


Figure 3. Comparison between the experimental yield (scaled by the initial reactant 2-picoline) of cyanoacetylene (points) and the predictions of the reaction model of Table I (line).

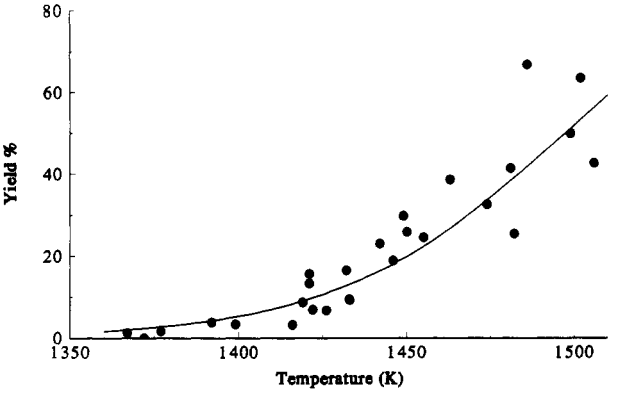


Figure 4. Comparison between the experimental yield (scaled by the initial reactant 2-picoline) of acetylene (points) and the predictions of the reaction model of Table I (line).

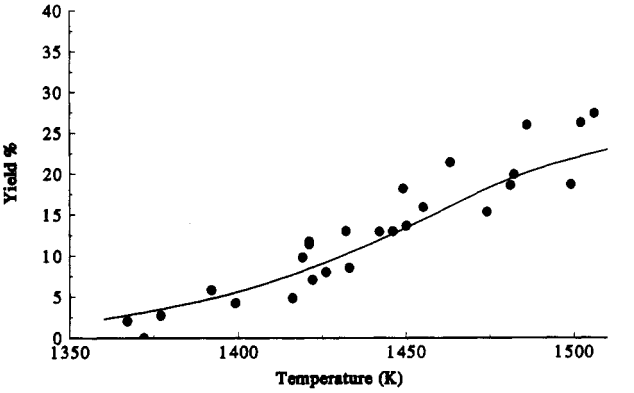


Figure 5. Comparison between the experimental yield (scaled by the initial reactant 2-picoline) of methane (points) and the predictions of the reaction model of Table I (line).

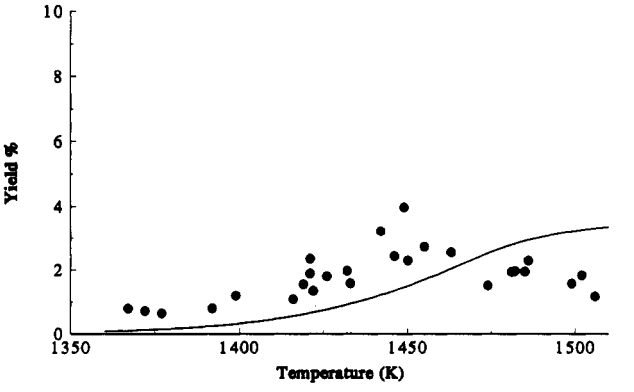


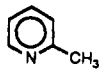
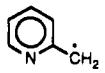
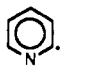
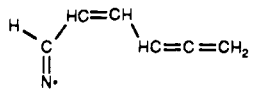
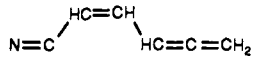
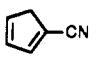
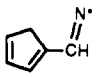
Figure 6. Comparison between the experimental yield (scaled by the initial reactant 2-picoline) of 1-cyanocyclopentadiene (points) and the predictions of the reaction model of Table I (line).

TABLE I: Reaction Model for 2-Picoline Pyrolysis[a]

	reaction	forward reaction log A	forward reaction n	forward reaction E	reverse reaction log A	reverse reaction n	reverse reaction E	ref
1	$PIC_2 \rightleftharpoons H + PYCH_2$	15.4	0	97.5	13.5	0	0.0	PW
2	$PIC_2 \rightleftharpoons A\text{-}C_5H_4N + CH_3$	16.1	0	91.5	12.6	0	0.0	PW
3	$CH_3 + PIC_2 \rightleftharpoons CH_4 + PYCH_2$	12.0	0	4.0	12.2	0	11.7	PW
4	$H + PIC_2 \rightleftharpoons H_2 + PYCH_2$	13.0	0	3.2	11.7	0	10.2	PW
5	$HCCHCN + PIC_2 \rightleftharpoons H_2CCHCN + PYCH_2$	12.6	0	2.5	12.5	0	10.8	est
6	$C_2H_3 + PIC_2 \rightleftharpoons C_2H_4 + PYCH_2$	12.6	0	1.5	13.1	0	9.8	PW
7	$NC_4H_3 + PIC_2 \rightleftharpoons C_4H_4 + PYCH_2$	12.3	0	2.5	12.4	0	12.8	PW
8	$PYCH_2 \rightleftharpoons L\text{-}C_6H_6NI$	15.3	0	80.0	11.7	0	6.9	PW
9	$A\text{-}C_5H_5 + HCN \rightleftharpoons L\text{-}C_6H_6NI$	11.9	0	5.0	13.8	0	6.3	PW
10	$L\text{-}C_6H_6NI \rightleftharpoons CVALL + H$	13.0	0	2.5	13.9	0	2.3	est
11	$CY\text{-}C_5H_5CN \rightleftharpoons CVALL$	15.4	0	77.9	13.3	0	50.0	est
12	$C_3H_3 + HCCHCN \rightleftharpoons CVALL$	12.0	0	0.0	15.8	0	84.9	est
13	$A\text{-}C_5H_5 \rightleftharpoons C_3H_3 + C_2H_2$	12.0	0	28.0	11.4	0	9.6	est
14	$A\text{-}C_5H_5 \rightleftharpoons CYC_5H_5$	11.0	0	8.0	15.6	0	63.7	est
15	$CYC_5H_5 + H \rightleftharpoons C\text{-}C_5H_6$	14.7	0	0.0	15.3	0	79.0	PW
16	$PIC_2 + CH_3 \rightleftharpoons O\text{-}CH_3PYR + CH_4$	12.3	0	11.0	12.6	0	6.6	PW
17	$PIC_2 + H \rightleftharpoons O\text{-}CH_3PYR + H_2$	13.0	0	8.0	11.8	0	2.9	PW
18	$O\text{-}CH_3PYR \rightleftharpoons B\text{-}C_5H_6CN$	14.5	0	35.0	10.6	0	8.5	est
19	$B\text{-}C_5H_5CN \rightleftharpoons A\text{-}C_5H_6CN$	12.3	0	5.0	12.9	0	10.9	est
20	$A\text{-}C_5H_6CN \rightleftharpoons C_3H_3 + H_2CCHCN$	14.0	0	24.0	12.7	0	4.2	est
21	$PIC_2 + CH_3 \rightleftharpoons CH_3PYR + CH_4$	12.0	0	8.5	12.3	0	4.1	PW
22	$PIC_2 + H \rightleftharpoons CH_3PYR + H_2$	13.0	0	7.0	11.8	0	1.9	PW
23	$CH_3PYR \rightleftharpoons NC_4H_3 + CH_3CN$	15.0	0	74.0	9.9	0	12.6	PW
24	$PIC_2 + CH_3 \rightleftharpoons C\text{-}CH_3PYR + CH_4$	12.0	0	12.0	12.3	0	7.6	PW
25	$PIC_2 + H \rightleftharpoons C\text{-}CH_3PYR + H_2$	13.0	0	12.0	11.8	0	6.9	PW
26	$C\text{-}CH_3PYR \rightleftharpoons C_6H_6NI$	15.0	0	70.0	11.9	0	10.3	est
27	$C_6H_6NI \rightleftharpoons D\text{-}C_5H_6CN$	13.0	0	3.0	12.4	0	35.3	est
28	$D\text{-}C_5H_6CN \rightleftharpoons CH_3 + CVA$	14.0	0	30.0	13.1	0	7.1	est
29	$PIC_2 + H \rightleftharpoons C_5H_5N + CH_3$	13.0	0	8.5	11.4	0	18.9	PW
30	$C_5H_5N \rightleftharpoons A\text{-}C_5H_4N + H$	15.9	0	102.0	14.1	0	0.0	19
31	$C_5H_5N + H \rightleftharpoons A\text{-}C_5H_4N + H_2$	13.5	0	5.0	12.3	0	7.5	19
32	$C_5H_5N + CH_3 \rightleftharpoons A\text{-}C_5H_4N + CH_4$	12.0	0	4.0	12.3	0	7.3	est
33	$A\text{-}C_5H_4N \rightleftharpoons C_4H_4CN$	14.0	0	40.0	11.7	0	8.6	19
34	$C_4H_4CN \rightleftharpoons C_2H_2 + HCCHCN$	13.2	0	37.0	10.9	0	2.4	19
35	$C_4H_4CN \rightleftharpoons CVA + H$	12.0	0	40.0	11.3	0	3.0	19
36	$C_4H_4CN \rightleftharpoons HCN + NC_4H_3$	13.7	0	45.0	11.0	0	4.9	19
37	$C_4H_4CN \rightleftharpoons A\text{-}C_4H_4CN$	13.0	0	18.0	12.1	0	23.9	est
38	$HCCCN + C_2H_3 \rightleftharpoons A\text{-}C_4H_4CN$	13.0	0	2.0	13.8	0	41.1	PW/19
39	$H + CVA \rightleftharpoons A\text{-}C_4H_4CN$	13.7	0	2.0	13.5	0	44.8	PW/19
40	$CVA + H \rightleftharpoons HCN + NC_4H_3$	13.5	0	3.0	11.5	0	−0.1	PW/19
41	$ETPYR \rightleftharpoons PYCH_2 + CH_3$	15.0	0	91.2	12.1	0	0.1	PW
42	$2PYCH_2 \rightleftharpoons (PYCH_2)_2$	12.3	0	0.0	15.7	0	76.2	est
43	$(C_5H_5)CHNI \rightleftharpoons CYC_5H_5 + HCN$	14.0	0	3.0	13.9	0	33.4	est
44	$(C_5H_5)CHNI \rightleftharpoons CY\text{-}C_5H_5CN + H$	13.6	0	1.5	13.9	0	5.0	est
45	$HCCHCN \rightleftharpoons HCCCN + H$	12.0	0	42.0	12.8	0	3.0	PW
46	$H + HCCHCN \rightleftharpoons H_2CCHCN$	13.3	0	0.0	15.2	0	105.7	est
47	$H + H_2CCHCN \rightleftharpoons HCN + C_2H_3$	13.0	0	4.0	11.1	0	4.1	19
48	$H + H_2CCHCN \rightleftharpoons HCCHCN + H_2$	13.7	0	8.0	12.4	0	6.7	est
49	$H_2CCHCN + M \rightleftharpoons HCCCN + H_2 + M$	16.7	0	80.0	16.2	0	39.7	est
50	$H + CH_3CN \rightleftharpoons CH_3 + HCN$	13.3	0	3.0	11.8	0	10.9	19
51	$C_4H_4 \rightleftharpoons 2C_2H_2$	15.2	0	81.1	13.7	0	44.4	35
52	$C_4H_4 \rightleftharpoons C_4H_2 + H_2$	14.3	0	87.0	13.3	0	45.1	35
53	$NC_4H_3 \rightleftharpoons C_4H_2 + H$	12.0	0	46.0	12.4	0	7.4	19
54	$C_2H_5(+M) \rightleftharpoons C_2H_4 + H(+M)$	13.3	0	39.7	12.5	0	2.0	36
55	$C_2H_4 + M \rightleftharpoons C_2H_2 + H_2 + M$	17.4	0	79.3	15.8	0	37.6	36
56	$C_2H_4 + M \rightleftharpoons C_2H_3 + H + M$	17.4	0	96.6	14.9	0	−9.2	est
57	$C_2H_4 + H \rightleftharpoons C_2H_3 + H_2$	13.7	0	8.0	11.8	0	6.7	37
58	$H + C_2H_2(+M) \rightleftharpoons C_2H_3(+M)$	13.0	0	2.7	12.7	0	43.1	38
59	$2CH_3(+M) \rightleftharpoons C_2H_6(+M)$	17.0	−1.18	0.7	16.1	0	84.7	39
60	$C_2H_6 + H \rightleftharpoons H_2 + C_2H_5$	2.7	3.5	5.2	14.5	0	21.4	40
61	$C_2H_6 + CH_3 \rightleftharpoons CH_4 + C_2H_5$	−0.3	4	8.3	14.8	0	26.6	40
62	$C_2H_2 + HCN \rightleftharpoons H_2CCHCN$	13.5	0	40.0	15.1	0	80.3	19
63	$CH_3 + H_2 \rightleftharpoons CH_4 + H$	2.8	3	7.7	15.1	0	16.9	40
64	$2C_3H_3 \rightleftharpoons C_4H_4 + C_2H_2$	12.7	0	0.0	13.7	0	38.4	32
65	$2C_3H_3 \rightleftharpoons L\text{-}C_6H_6$	12.7	0	0.0	15.0	0	58.4	32
66	$L\text{-}C_6H_6 \rightleftharpoons C_6H_6$	12.0	0	33.0	16.9	0	115.9	32
67	$HCCHCN \rightleftharpoons C_2H_2 + CN$	14.7	0	58.0	13.8	0	1.0	PW
68	$CN + H_2 \rightleftharpoons HCN + H$	5.7	2.44	2.1	15.0	0	27.1	41
69	$C_2N_2 + M \rightleftharpoons 2CN + M$	16.9	0	100.4	14.3	0	−28.8	42
70	$H + C_2N_2 \rightleftharpoons HCN + CN$	14.5	0	7.9	13.1	0	1.2	43

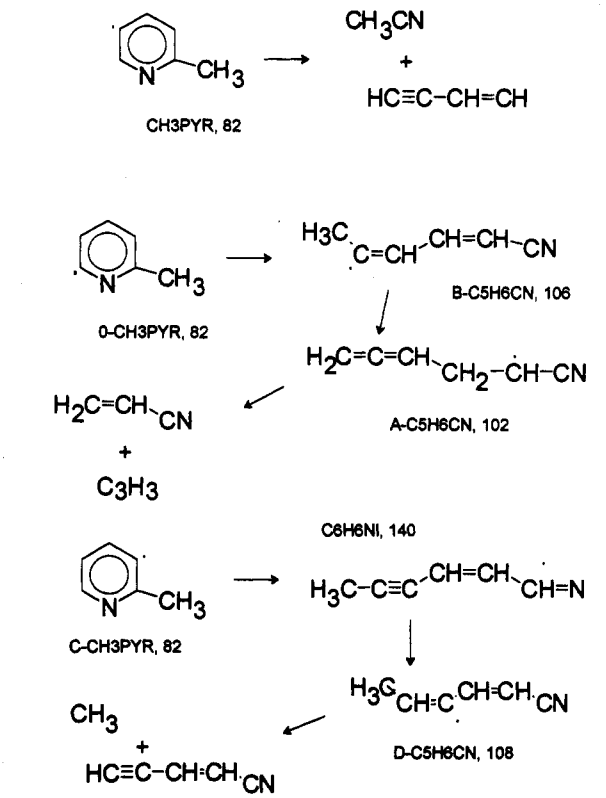
[a] Units for A, $cm^3\ mol^{-1}\ s^{-1}$ or s^{-1} as appropriate. Units for E, kcal mol^{-1}. PW indicates rate constant evaluated in the present work; est indicates rate constant estimated in the present work.

TABLE II: Thermochemical Parameters for the 2-Picoline System

structure	name[a]	$\Delta H°_{f,300}$, kcal/mol	$S°_{300}$, cal/(K mol)	$C°_p$, cal/(K mol) 300	500	1000	1500	2000
	PIC2[b]	23.7	77.8	24.1	38.8	58.7	67.3	71.5
	PYCH2	68	78.1	25.4	38.8	56.3	63.9	67.4
	A-C5H4N	84.1	72.6	18.0	28.9	42.8	48.5	67.4
	L-C6H6NI	140	91.5	31.8	42.8	55.4	62.9	66.6
	CVALL	89.3	82.2	28.4	39.9	52.3	58.2	61.6
	CY-C5H5CN	63.7	77.0	22.7	35.2	51.9	56.9	59.1
	(C5H5)CHNI	118	82.6	26.3	39.1	55.2	61.8	64.0

[a] Name as shown in Table I. [b] Heat of formation from ref 21, entropy and heat capacities calculated from ref 30.

SCHEME V: Postulated Mechanisms from Ring Opening of Methylpyridyls. The Name of the Species Shown in Table I Is Indicated Together with the Heat of Formation (kcal mol^{-1}) at 300 K



was predicted within a factor of 2 of the experimental yields and ethylene within a factor of 3.

The initiation rates for 2-picoline included in Table I (reactions 1 and 2) are the result of optimization to fit experimental data. Sensitivity analysis indicated that the overall rate of disappearance of 2-picoline was very sensitive to the initiation route yielding methyl and *o*-pyridyl (reaction 2). Methane and cyanoacetylene were also very sensitive to the rate of initiation by reaction 2. Optimization of both the Arrhenius preexponential factor and the activation energy of this reaction allowed the heat of formation of the *o*-pyridyl to be derived. The heat of formation for *o*-pyridyl obtained in this manner was 84.1 (±2) kcal mol^{-1}, in excellent agreement with previously published values.[19,29]

Determining the rate constant for decomposition of 2-picoline to yield H atoms and 2-picolyl (reaction 1) proved to be difficult. The mechanism exhibited little sensitivity to the rate of this reaction. This could be explained by rate of production analysis which showed that the dominant means of generation of 2-picolyl radicals was through H abstraction by methyl radicals. The rate of recombination of H atoms and 2-picolyl (reaction −1) did, however, influence the rate of decomposition of 2-picoline. The kinetic model suggested that 2-picolyl might act as a radical trap in the pyrolysis, with faster rates of recombination resulting in a slower rate of decomposition of 2-picoline. This sensitivity allowed reaction −1 to be optimized, yielding a final value of 3×10^{13} cm^3 mol^{-1} s^{-1} (range of uncertainty 1×10^{13}–6×10^{13}).

Although the kinetic model did not show sensitivity to the initiation reaction 1, the rate of the forward reaction can be calculated from the recombination rate constant k_{-1}. The thermochemistry of 2-picolyl must be known for this to be possible. Although there is uncertainty as to the heat of formation of the 2-picolyl radical, statistical mechanical methods[20] can be used to obtain relatively reliable values for the entropy and heat capacity of 2-picolyl. Vibrational frequencies for 2-picolyl were estimated from 2-picoline frequencies by examining the differences in vibrational frequencies between toluene and benzyl.[13] Where no change in frequency is observed, the corresponding vibrational frequency of 2-picoline was used.[30] If the mode exhibited a change in frequency, the same fractional change as observed in benzyl compared to toluene was used. The heat capacity and entropy functions therefore allow the Arrhenius preexponential factor for reaction 1 to be calculated from its reverse reaction −1. Since the recombination reaction −1 is independent of the uncertain heat of formation of 2-picolyl, the Arrhenius preexponential factor of reaction 1 can be considered not to include this source of uncertainty.

The major route for the decomposition of 2-picolyl in the kinetic model is the ring opening reaction discussed previously (see Scheme III). This reaction is included as reaction 8 of the model. The Arrhenius preexponential factor for this reaction was chosen by analogy with the ring opening reaction of furan.[31,32] Rate of production analysis showed the decomposition of the iminyl radical formed in reaction 8 to yield open chain C_5H_5 and HCN accounted for approximately 70% of the HCN observed in the decomposition of 2-picoline. At moderate to high extents of decomposition, the yield of HCN predicted by the model had a sensitivity coefficient of approximately 0.7 to reaction 8 (see Table III). Assuming the estimated heat of formation of the open chain iminyl radical

TABLE III: Sensitivity Coefficients in the 2-Picoline System for Selected Products Evaluated at 1430 K and at 250 μs

	normalized sensitivity coefficients									
reaction no.	PIC_2	HCCCN	HCN	H_2CCHCN	CH_3CN	C_5H_5N	$(C_5H_5)CN$	CH_4	C_2H_2	C_5H_6
1	−0.0015									
−1	−0.0040		−0.044			−0.068				−0.104
2	−0.0848	0.954	0.755	0.828	0.775	0.843	0.609	0.800	0.963	1.235
3	−0.0044		0.085	−0.275	−0.249		0.182	0.195		
4				−0.281	−0.311	−0.548	0.128	−0.044		
6				−0.074	−0.082	−0.145	0.035	−0.025	−0.156	
8			0.699				0.945		0.031	0.954
9	0.0011		0.233			−0.039	−0.666			0.289
10			−0.229			0.039	0.669			−0.284
13									0.025	−0.251
15										0.541
16			0.056	0.477	−0.041			0.036	0.034	
17				0.405	−0.056	−0.099	−0.031		0.029	
21	−0.0021				0.398			0.032		
22	−0.0016			−0.046	0.425	−0.101				
23	−0.0021				0.703					
24								0.034		
29	−0.0021					0.909		0.056		
38		0.102							0.078	
39		−0.085							−0.076	
41								−0.033		
42			−0.079				−0.108			−0.102
58				0.067	0.072	0.132			0.147	
59				−0.040						
62			0.140	−0.085						
64									0.028	

to be accurate to ±3 kcal mol^{-1}, the activation energy for ring opening can be used to determine a value for the heat of formation of 2-picolyl. Using this approach, the heat of formation of 2-picolyl at 300 K was determined to be 68 (±5) kcal mol^{-1}. It should be noted that the heat of formation determined in this manner is dependent on the correctness of the proposed pathway for 2-picolyl decomposition.

A heat of formation of 2-picolyl of 68 (±5) kcal mol^{-1} implies that 2-picolyl is significantly less resonance stabilized than benzyl. This is supported by our rate of H and 2-picolyl recombination determined from modeling. Over the temperature range of 300–1650 K recombination of benzyl and H atoms has been found to be temperature independent,[6] with a rate constant of 2.5 (±0.8) × 10^{14} cm^3 mol^{-1} s^{-1}. This is much higher than what might be considered to be the "normal" upper limit[19,20] for radical recombination reactions of 5 × 10^{13} cm^3 mol^{-1} s^{-1}. This high rate of recombination could be a result of the resonance stabilization of the benzyl radical. The observation that the recombination rate for 2-picolyl is closer to this "normal" value gives some support for our high value for the heat of formation of 2-picolyl, and the postulate that 2-picolyl may indeed be significantly less resonance stabilized than benzyl.

Rates for reactions of the C_5H_5 radical formed in reaction 9 were difficult to estimate due to the lack of precedence for fission of this radical into acetylene and propargyl (reaction 13). Both acetylene and propargyl are fairly rigid species, and hence a low Arrhenius preexponential factor was used for this reaction. It should be noted that the only product showing significant sensitivity to this fission was the minor product cyclopentadiene. Cyclopentadiene was formed in the model through cyclization of C_5H_5 (Scheme III), and therefore the rate of the competing fission route influences the predicted yield of cyclopentadiene.

Another reaction found to influence the predicted yield of cyclopentadiene was the recombination rate of H atoms and cyclopentadienyl radicals (reaction 15). A final value of $10^{14.7}$ cm^3 mol^{-1} s^{-1} was used in the model. If the high recombination rate for benzyl radicals results from their resonance stabilization,[6] then the resonance stabilized cyclopentadienyl might also undergo rapid recombination with H. Its rate constant would be expected to be higher than that of benzyl owing to the five-fold degeneracy for H addition to cyclopentadienyl.

The reaction rates for the minor pathways resulting in the formation of 1-cyanocyclopentadiene were determined from thermochemistry and by analogy with hydrocarbon systems. The Arrhenius preexponential factor for the cyclization of cyanovinylallene to 1-cyanocyclopentadiene (reaction 11) was calculated from the reverse reaction which would be expected to possess a large A factor. An additional 5 kcal mol^{-1} was added to the energy required to form the biradical, as suggested from Benson's conclusions regarding the biradical mechanism.[20] Reaction 12 of the kinetic model is an alternative fate to cyclization for cyanovinylallene. This high activation energy fission reaction may partly account for the decomposition of 1-cyanocyclopentadiene.

The decomposition of 1-cyanocyclopentadiene through a H addition mechanism is included in reactions 44 and 45 of the model. The rate constants for this pathway were determined from the thermochemistry of the H adduct (species (C5H5)CHNI in Table II), rates of H addition to the cyano carbon of 1-cyanocyclopentadiene, and fission of the adduct. The rates of these steps were chosen to be those proposed for analogous reactions of nitriles.[33]

Radical recombination reactions would be expected to be important for the 2-picolyl radical considering the relatively high concentrations which would be anticipated in the pyrolysis of 2-picoline. Recombination of benzyl radicals has been recently found to be an important mechanism for the disappearance of benzyl at low temperatures.[7] The production of H atoms through the decomposition of dibenzyl to stilbene was also found to affect the stoichiometry of the generation of H atoms.[7] The recombination of 2-picolyl radicals is included in the model as reaction 43. Rate of production analysis indicated that 2-picolyl and 2,2-dipicolyl reached equilibrium rapidly, resulting in a predicted maximum yield of 4.5% at 1460 K. This would be observable only as a loss of nitrogen from the system, due to the involatility of this product species. Although there is considerable scatter in the mass balance data presented previously,[1] preventing definite conclusions being made, such a loss of mass is not inconsistent with the experimental data. The mass balances for the pyrolysis of 2-picoline appear to pass through a minimum at 1400–1450 K.

Decomposition reactions of 2,2-dipicolyl are not included in the model. This simplification was seen as necessary since the actual concentrations of 2-picolyl could not be observed other than indirectly through mass balance data. This modeling study does not appear to be sensitive to the change in H atom stoichiometry resulting from the omission of these reactions.

Another recombination reaction which might be thought to be of importance in the pyrolysis of 2-picoline is the reaction between

methyl and 2-picolyl radicals (reaction 42). Experimentally, only traces of the expected product, ethylpyridine, were observed.[1] To model this, a low rate of recombination (compared with rates measured for the recombination of methyl and benzyl[2]) was required. Modeling of ethylpyridine is complicated, however, by the possibility of its decomposition, uncertainties in the thermochemistry, and difficulties in quantifying the yield of high boiling point reaction products.

Decomposition reactions for the *o*-pyridyl radical were taken from the previously published model for pyridine decomposition.[19] The mechanism was modified, however, to account for a discrepancy in the ethylene predicted using the reactions taken from the earlier pyridine model. Abstraction by vinyl radicals in the pyridine case would be expected to be close to thermoneutral, whereas H abstraction by vinyl from 2-picoline to yield 2-picolyl would be expected to be exothermic. This could result in abstraction by vinyl being of little importance in the decomposition of pyridine but result in the formation of ethylene in the decomposition of 2-picoline.

Unless there is the possibility of a rapid abstraction route for vinyl formed in the decomposition of *o*-pyridyl, vinyl radicals would undergo unimolecular decomposition to yield acetylene and H atoms. The two major pathways for the decomposition of *o*-pyridyl[19,20] result in the formation of acetylene and cyanovinyl, or alternatively, the formation of vinyl and cyanoacetylene. If there is no rapid H-abstraction route for vinyl radicals possible, it would not be possible to distinguish the relative rates of the two routes.

A more complete mechanism for *o*-pyridyl decomposition was found to be necessary in the 2-picoline kinetic model. In the original decomposition mechanism for pyridine, *o*-pyridyl ring opened to the C_4H_4CN radical. This radical then decomposed to yield acetylene and cyanovinyl, or vinyl and cyanoacetylene. This represents a simplification of the pathway, as the C_4H_4CN radical must first undergo a 1,4 H shift prior to fission to vinyl and cyanoacetylene. This type of hydrogen shift would be expected to proceed with a low barrier,[34] and the Arrhenius preexponential factor reflects the "tight" transition state required for such a rearrangement (reaction 33). The modified pyridine submechanism appears in reactions 31–40 of the kinetic model.

H-abstraction reactions from the side chain of 2-picoline are included in reactions 3–7 of the kinetic model. The temperature range over which modeling was carried out was too narrow to allow the temperature dependence of the abstraction reactions to be determined, and therefore activation energies may not be of physical relevance. H abstraction by methyl appears to occur faster by approximately a factor of 3 than is usually expected.[19,34] The major product, methane, appeared to be sensitive to the rate constant for abstraction: slower rates of abstraction resulted in underprediction of the methane and also considerable overprediction of the termination product, ethane. H-abstraction from the 2-picoline ring was found to proceed considerably slower than abstraction of picolyllic hydrogens, most likely as a consequence of these abstractions being endothermic.

Sensitivity and Rate of Production Analysis. Sensitivity and rate of production analysis can give insight into the role of individual reactions forming part of a complex mechanism. The results of this analysis should however, be interpreted with caution, since their relevance to the decomposition of 2-picoline depends on the correctness of the kinetic model. Sensitivity data for major products are tabulated in Table III. For the species HCN and acetylene, temperature profiles of the sensitivity coefficients of the most sensitive reactions are given in Figures 7 and 8.

An interesting feature of the decomposition of 2-picoline is the importance of the initiation reaction yielding methyl and *o*-pyridyl radicals. Rate of production analysis reveals that 27% of the 2-picoline decomposes unimolecularly through this initiation reaction. A large proportion of 2-picoline therefore decomposes through a radical pathway which is not a chain mechanism.

Sensitivity analysis also reflects the importance of the initiation reaction 2 (see Table III). All products originating from *o*-pyridyl have a sensitivity of close to 1 for this reaction. This is not typical

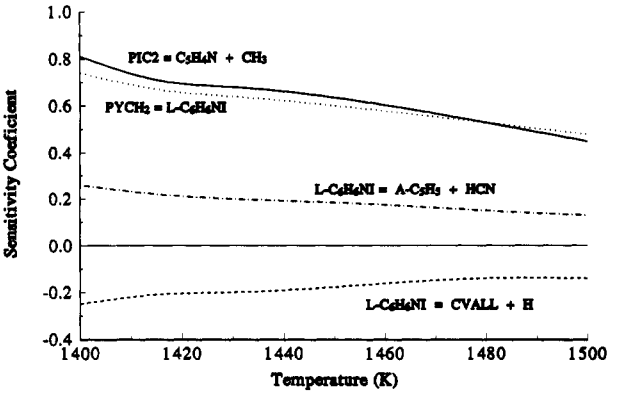


Figure 7. Variation with temperature of the sensitivity coefficients for HCN. Only the most sensitive reactions from Table I are shown.

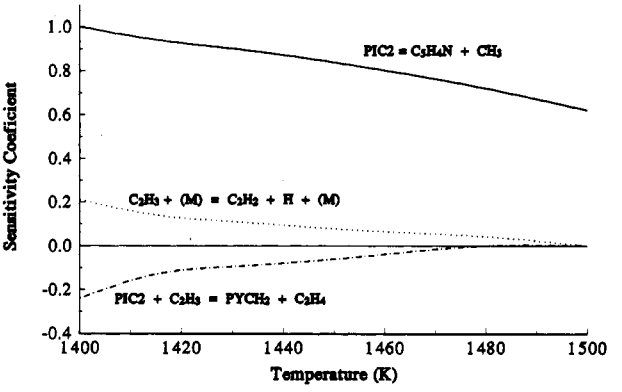


Figure 8. Variation with temperature of the sensitivity coefficients for acetylene. Only the most sensitive reactions from Table I are shown.

of free-radical chain mechanisms, whose sensitivities tend to be dominated by initiation reactions only at low extents of decomposition. Products whose rates of formation are dependent on methyl radical concentration to an order of greater than unity were found to possess sensitivities to reaction 2 of greater than 1. Examples of this behavior include ethane, with a sensitivity coefficient of 1.71 at 1430 K and 300 μs.

Sensitivity analysis at various temperatures revealed very little change over the temperature range studied. A typical example of this behavior is shown in the sensitivity profile of acetylene included in Figure 8. An exception to this is the sensitivity of HCN, where the rate of 2-picolyl ring cleavage (reaction 8) has comparible sensitivity to initiation reaction 2. An interesting feature of the sensitivity profile for HCN (Figure 7) is the "mirror imaging" of the profiles for the two competing reactions 9 and 10.

It must be seen as fortunate that the decomposition of 2-picoline produces products which can readily be assigned as arising mainly from either the *o*-pyridyl or from the 2-picolyl route. The sensitivity of HCN predicted by the model to the rate of 2-picolyl decomposition has allowed proposals to be made on the stability of the 2-picolyl radical. This is in contrast to the toluene case, where the products arising from phenyl radicals and those arising from benzyl were not readily distinguishable, leading to difficulty in assessing the relative importance of the two pathways.

Conclusion

The thermal decomposition of 2-picoline has been successfully modeled using a 70-reaction mechanism. Modeling showed that decomposition proceeded mainly by two parallel pathways which stemmed from the two possible initiation reactions of 2-picoline. Loss of methyl from 2-picoline to yield *o*-pyridyl radicals resulted in the formation of the major products cyanoacetylene, acetylene, and methane. The rate of this initiation reaction was found by sensitivity analysis to greatly influence the overall rate of decomposition of 2-picoline and, importantly, the rate of formation of the 2-picolyl radical.

Elucidation of the mechanism of 2-picolyl decomposition was assisted by the deduction that the products HCN, 1-cyanocyclopentadiene, and cyclopentadiene are formed principally from the 2-picolyl route. The kinetics of HCN formation were found to be consistent with the direct ring opening of 2-picolyl. The minor product 1-cyanocyclopentadiene was proposed to form by isomerization of cyanovinylallene, produced from the decomposition of 2-picolyl.

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Registry No. NO_x, 11104-93-1; 2-picoline, 109-06-8; 2-picolyl, 52962-96-6.

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