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Thermal Decomposition and Ring Expansion in 2,4-Dimethylpyrrole. Single Pulse Shock Tube and Modeling Studies

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The thermal decomposition of 2,4-dimethylpyrrole was studied behind reflected shock waves in a pressurized driver single-pulse shock tube over the temperature range 1050−1250 K at overall densities of $\sim 3 \times 10^{-5}$ mol/cm^3. A plethora of decomposition products, both with and without nitrogen, were found in the post-shock mixtures. They were, among the nitrogen containing products: pyridine, two isomers of methylpyrrole, 2-picoline, 5-picoline, HCN, CH_3CN, C_2H_3CN, C_2H_5CN, and $CH{\equiv}C{-}CN$. Very small quantities of *cis*- and *trans*-$CH_3CH{=}CHCN$ and $CH_2{=}CHCH_2CN$ were also found in the post-shock mixtures. Among the products without nitrogen were CH_4, C_2H_4, C_2H_6, C_2H_2, $CH_3C{\equiv}CH$, $CH_2{=}C{=}CH_2$, C_4H_4 and C_4H_2, and very small quantities of other C_4 hydrocarbons and C_5 hydrocarbons. The initiation of a chain mechanism in the decomposition of 2,4-dimethylpyrrole takes place via ejection of hydrogen atoms from sp^3 carbons and dissociation of the two methyl groups attached to the ring. The H atoms and the methyl radicals initiate a chain mechanism by abstraction of a hydrogen atom from the methyl group and by dissociative recombination of an H atom and removal of a methyl group from the ring. In addition to the dissociation reactions, there are several unimolecular channels that involve ring cleavage. Ring expansion processes that lead to the production of high yields of pyridine and picoline take place from radical species: $CH_3[C_4H_2NH]CH_2^{\bullet}$ in the production of picoline and $[C_4H_3NH]CH_2^{\bullet}$ in the production of pyridine. In addition to the chain mechanism, there are unimolecular breakdown processes of the pyrrole ring to yield stable products such as HCN, CH_3CN, and others. The total decomposition of 2,4-dimethylpyrrole in terms of a first-order rate constant is given by $k_{\text{total}} = 10^{16.31} \exp(-75.7 \times 10^3/RT)$ s^{-1}. A reaction scheme containing 36 species and 69 elementary reactions was composed and a computer simulation was performed over the temperature range 1050−1250 K at 25 K intervals. The agreement between the experimental results and the model prediction for most of the species is satisfactory

I. Introduction

The thermal reactions of pyrrole[1−5] and its methyl derivatives[6−8] have been thoroughly investigated in the past by several groups of investigators. Experimental results, modeling, and quantum chemical calculations of potential energy surfaces have been published. In addition to fragmentation of the molecules when subjected to shock heating, two major types of reactions take place. In pyrrole, the isomerizations to cis and trans crotonitrile and vinyl acetonitrile are major reaction channels, whereas in the various isomers of methylpyrrole, ring expansion to form pyridine is a major step. The ring expansion processes in all methylpyrrole isomers take place via methylene pyrrole radicals as intermediates.[7] Except for isomerizations resulting from migrations of the methyl group, no other isomerizations in methylpyrrole were reported. Experimental results, modeling, and quantum chemical calculations have also been published on the thermal reactions of indole which is pyrrole fused to benzene.[9−12] In this molecule too, the major reactions are isomerizations that take place either from indole or from its 3-indolenine tautomer.

As far as we are aware, the thermal reactions of either dimethylpyrrole or dimethylindole have never been studied in the past. 2,4-Dimethylpyrrole is an asymmetrical molecule that can yield upon ring expansion 2-picoline and 5-picoline. It may also fragmentize to yield smaller molecules both with and without nitrogen.

In the present investigation, the thermal reactions of 2,4-dimethylpyrrole are reported, a mechanism for the production of the decomposition products is suggested, and a computer simulation is performed to verify the suggested reaction scheme.

II. Experimental Section

A. Apparatus. The decomposition of 2,4-dimethylpyrrole was studied behind reflected shock waves in a pressurized driver, heated, 52 mm i.d. single-pulse shock tube. The tube, made of electropolished stainless steel tubing, was heated and maintained at 110 °C with variation of ∼±1 °C. The 4 m long driven section was divided in the middle by a 52 mm i.d. ball valve. The driver had a variable length up to a maximum of 2.7 m and could be varied in small steps in order to obtain the best cooling conditions. A 36 L dump tank was connected to the driven section at a 45° angle near the diaphragm holder in order to prevent reflection of transmitted shocks. The driven section was separated from the driver by a "Mylar" polyester film of various thicknesses depending upon the desired shock strength.

After pumping down the tube to approximately 3×10^{-5} Torr, the reaction mixture was introduced into the section between the valve and the end plate and pure argon into the section between the diaphragm and the valve, including the dump tank. After running an experiment, samples were trans-

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ferred from the downstream end of the driven section into a Hewlett-Packard model 5890 gas chromatograph operating with two Porapak-N columns using flame ionization (FID) and nitrogen-phosphor (NPD) detectors. All of the transfer tubes and the injection system were maintained at 110 °C.

Reflected shock temperatures were calculated from the extent of decomposition of 1,1,1-trifluoroethane that was added to the reaction mixture in small quantities and served as an internal standard. Its decomposition to $CH_2{=}CF_2 + HF$ is a first-order unimolecular reaction with a rate constant[13] $k_{\text{first}} = 10^{14.85}\exp(-74.05 \times 10^3/RT)\ s^{-1}$.

Reflected shock temperatures were calculated from the measured extent of reaction, using the relation

$$T = -(E/R)/\left[\ln\left\{-\frac{1}{At}\ln(1-\chi)\right\}\right] \qquad \text{(I)}$$

where E is the activation energy of the HF elimination, A is its preexponential factor, t is the reaction dwell time, and χ is the extent of decomposition defined as

$$\chi = [CH_2{=}CF_2]_t/([CH_2{=}CF_2]_t + [CH_3CF_3]_t) \qquad \text{(II)}$$

The additional reflected shock parameters were calculated from the measured incident shock velocities using the three conservation equations and the ideal gas equation of state. Dwell times of approximately 2 ms were measured with an accuracy of ~5%. Cooling rates were approximately 5×10^{-5} K/s.

B. Materials and Analysis. Reaction mixtures containing 0.3% 2,4-dimethylpyrrole and 0.1% 1,1,1-trifluoroethane diluted in argon were prepared manometrically and stored in 12 L glass bulbs at 700 Torr. Both the bulbs and the gas manifold were pumped down to $\sim 10^{-5}$ Torr before the preparation of the mixtures. 2,4-Dimethylpyrrole was obtained from Aldrich Chemical Co. and was listed as 97% pure. However, chromatograms of unshocked samples did not show products that appeared in the shocked samples. The argon used was Matheson ultrahigh purity grade, listed as 99.9995%, and the helium was Matheson pure grade, listed as 99.999%.

The gas chromatographic analyses of the pre and post-shock mixtures were performed on two 2 m Porapak-N columns using flame ionization and nitrogen−phosphor detectors. The initial column temperature of 35 °C was gradually elevated to 190 °C in an analysis that lasted approximately 2.5 h. Typical chromatograms of 0.3% 2,4-dimethylpyrrole in argon of a shock heated mixture to 1170 K taken on a FID and NPD are shown in Figure 1.

C. Determination of Product Concentrations. The concentrations of the reaction products $C_5(\text{pr})_i$ were calculated from their GC peak areas from the following relations:

$$C_5(\text{pr})_i = A(\text{pr}_i)_t/S(\text{pr}_i)\{C_5(\text{2,4-dimethylpyrrole})_0\}/A(\text{2,4-dimethylpyrrole})_0 \qquad \text{(III)}$$

$$C_5(\text{2,4-dimethylpyrrole})_0 = \{p_1\ \%(\text{2,4-dimethylpyrrole})\rho_5/\rho_1\}/100RT_1 \qquad \text{(IV)}$$

$$A(\text{2,4-dimethylpyrrole})_0 = A(\text{2,4-dimethylpyrrole})_t + 1/6\Sigma N(\text{pr}_i)\ A(\text{pr}_i)_t/S(\text{pr}_i) \qquad \text{(V)}$$

In these relations that are based on carbon atom conservation, $C_5(\text{2,4-dimethylpyrrole})_0$ is the concentration of 2,4-dimethylpyrrole behind the reflected shock wave prior to decomposition and $A(\text{2,4-dimethylpyrrole})_0$ is the calculated GC peak area of 2,4-dimethylpyrrole prior to decomposition (eq V) where $A(\text{pr}_i)_t$ is the peak area of a product i in the shocked sample, $S(\text{pr}_i)$ is its sensitivity relative to 2,4-dimethylpyrrole, and $N(\text{pr}_i)$ is the number of its carbon atoms. ρ_5/ρ_1 is the compression behind the reflected shock wave, and T_1 is room temperature, 110 °C in this study.

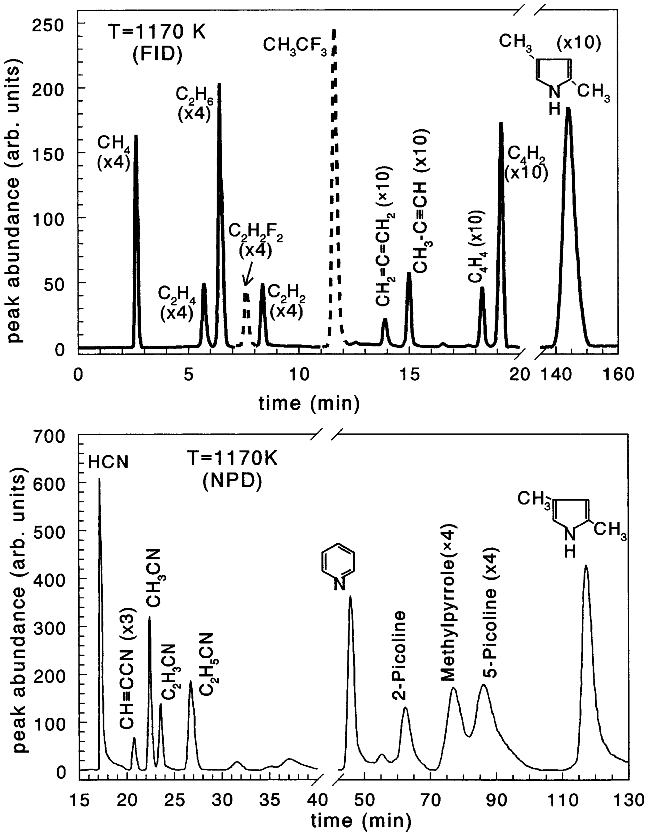


Figure 1. Gas chromatograms of a shock sample of 0.3% 2,4-dimethylpyrrole and 0.1% 1,1,1-trifluoroethane in argon, heated to 1170 K. (a) species without nitrogen, (b) species with nitrogen. The numbers on the chromatograms are multiplication factors.

The identification of reaction products in the GC was based on their retention times and on analyses with a Hewlett-Packard model 5970 mass selective detector. The sensitivities of the various products to the FID and NPD were determined relative to 2,4-dimethylpyrrole from standard mixtures. The areas under the GC peaks were integrated with a Spectra Physics model SP4200 computing integrator and were transferred after each analysis to a PC for data reduction and graphical presentation.

III. Results

To determine the distribution of reaction products, some 30 tests were run with mixtures containing 0.3% 2,4-dimethylpyrrole and 0.1% 1,1,1-trifluoroethane in argon, covering the temperature range 1050−1250 K. Trifluoroethane served as an internal standard for temperature determination. Extents of pyrolysis starting from a few hundredths of one percent were determined for many of the products. Details of the experimental conditions and the distribution of reaction products are given in Table 1 and are shown graphically in Figures 2 and 3. The percent of a given product in the table, corresponds to its mole fraction in the post-shock mixture (not including Ar and H_2), irrespective of the number of its carbon atoms. Products of very small quantities such as C_4 compounds other than C_4H_4 and C_4H_2 and C_5 hydrocarbons were not included in the list of reaction products.

TABLE 1: Experimental Conditions and Product Distribution (in Mole Percent) of Products without and with Nitrogen in the Decomposition of 2,4-Dimethylpyrrole

Products without Nitrogen

no.	T_5(K)	$C_5 \times 10^5$	t(ms)	DMP	CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_4	C_4H_4	C_4H_2
1	1073	2.65	1.42	98.12	0.675	0.0255	0.173		0.0141	0.0073	0.0135
2	1083	2.80	1.47	97.10	1.14	0.0423	0.314	0.0098	0.0226	0.0113	0.0266
3	1101	2.72	1.27	95.58	1.49	0.0566	0.500	0.0166	0.0430	0.0151	0.0416
4	1107	2.85	1.34	94.97	1.71	0.0411	0.616	0.0160	0.0359	0.0181	0.0683
5	1114	2.65	1.70	93.17	2.24	0.0650	0.959	0.0260	0.050	0.0274	0.107
6	1114	2.35	1.84	91.36	3.13	0.115	1.25	0.0355	0.0689	0.0368	0.151
7	1121	2.51	2.0	88.75	3.70	0.177	1.90	0.0592	0.112	0.0472	0.211
8	1123	2.32	2.0	87.41	3.58	0.190	2.01	0.0670	0.118	0.0514	0.233
9	1123	2.45	1.55	88.88	3.04	0.177	1.48	0.0743	0.176	0.0375	0.109
10	1124	2.26	2.07	87.71	4.54	0.234	2.60	0.0824	0.144	0.0619	0.0289
11	1134	2.34	1.99	82.89	4.97	0.297	3.06	0.110	0.176	0.0742	0.352
12	1140	2.78	1.50	85.61	4.14	0.234	2.11	0.0848	0.145	0.0587	0.263
13	1142	2.59	2.0	80.07	5.33	0.323	3.28	0.127	0.178	0.0882	0.411
14	1153	2.44	1.50	80.21	5.13	0.363	3.20	0.141	0.224	0.0907	0.392
15	1156	2.72	1.70	78.0	5.50	0.385	3.58	0.163	0.217	0.101	0.464
16	1156	2.55	1.40	78.91	5.91	0.409	3.78	0.161	0.237	0.104	0.469
17	1157	2.39	2.0	68.14	9.12	0.810	6.86	0.389	0.454	0.198	0.951
18	1157	2.52	1.80	72.98	6.67	0.577	4.99	0.266	0.297	0.152	0.706
19	1166	2.67	1.71	71.05	6.95	0.562	4.77	0.256	0.298	0.142	0.665
20	1166	2.59	1.60	69.71	7.18	0.603	4.83	0.274	0.326	0.149	0.696
21	1166	2.38	1.60	67.30	6.66	0.744	4.61	0.361	0.573	0.150	0.512
22	1170	2.55	1.50	68.29	7.43	0.643	5.10	0.293	0.336	0.157	0.735
23	1182	2.46	1.60	59.78	7.86	0.933	6.12	0.453	0.547	0.214	0.904
24	1190	2.40	2.18	42.42	10.65	1.71	9.51	1.07	0.775	0.374	1.72
25	1193	2.47	1.50	50.11	10.43	1.39	9.10	0.776	0.70	0.310	1.44
26	1199	2.32	2.0	35.45	12.80	2.26	11.77	1.47	1.06	0.466	2.14
27	1203	2.43	1.89	38.21	11.46	2.42	10.54	1.76	1.02	0.491	2.19
28	1205	2.40	1.90	30.91	14.45	2.78	13.46	1.97	1.20	0.538	2.52
29	1225	2.58	1.75	24.21	12.66	3.01	12.06	2.28	1.20	0.610	2.53
30	1235	2.39	1.61	17.09	13.96	3.71	13.95	2.96	1.48	0.734	3.01
31	1250	2.55	1.68	12.98	12.0	4.18	11.50	3.77	1.53	0.773	2.80

Products with Nitrogen

no.	T_5(K)	DMP	HCN	CHCCN	CH_3CN	C_2H_3CN	C_2H_5CN	pyridine	MP	2-picoline	5-picoline
1	1073	98.12	0.0302		0.0247	0.0031		0.146	0.0918	0.436	0.242
2	1083	97.10	0.0232		0.0422	0.0052		0.242	0.0803	0.622	0.312
3	1101	95.58	0.0457		0.0795	0.0087	0.0024	0.472	0.154	1.05	0.444
4	1107	94.97	0.0251		0.0788	0.0057	0.0039	0.521	0.411	1.09	0.395
5	1114	93.17	0.0425		0.117	0.0026		0.823	0.383	1.55	0.440
6	1114	91.36	0.0407		0.127	0.0101	0.0075	1.02	0.273	1.82	0.538
7	1121	88.75	0.122		0.190	0.0283	0.0121	1.16	0.665	1.95	0.911
8	1123	87.41	0.140		0.194	0.0252	0.0161	1.56	0.751	2.31	1.34
9	1123	88.88	0.221		0.268	0.0842	0.0089	1.40	0.210	2.71	1.13
10	1124	87.71	0.154		0.195	0.0274	0.0173	1.25	0.553	1.94	0.454
11	1134	82.89	0.283		0.298	0.0414	0.0295	2.20	1.03	2.96	1.23
12	1140	85.61	0.264	0.00079	0.254	0.0293	0.0182	1.95	0.695	2.83	1.31
13	1142	80.07	0.342	0.00089	0.325	0.0379	0.0290	3.01	1.09	3.68	1.67
14	1153	80.21	0.353		0.40	0.0639	0.0403	2.98	0.870	3.66	1.88
15	1156	78.0	0.336		0.405	0.0609	0.0457	3.34	1.26	4.01	2.13
16	1156	78.91	0.454	0.0040	0.378	0.0536	0.0385	3.11	0.654	3.74	1.59
17	1157	68.14	0.432	0.0172	0.616	0.151	0.106	4.39	0.964	4.90	1.51
18	1157	72.98	0.386	0.0044	0.561	0.107	0.0859	4.53	1.11	4.85	1.73
19	1166	71.05	0.468	0.00370	0.555	0.0944	0.0763	4.76	1.52	5.17	2.66
20	1166	69.71	0.707	0.0034	0.582	0.0933	0.0695	5.19	1.63	5.29	2.66
21	1166	67.30	1.22	0.0040	0.863	0.313	0.0860	5.31	1.68	6.27	3.34
22	1170	68.29	0.831	0.0039	0.657	0.109	0.0798	5.67	1.45	5.53	2.68
23	1182	59.78	1.04	0.0082	0.924	0.254	0.159	8.02	2.13	6.98	3.67
24	1190	42.42	1.49	0.0299	1.21	0.393	0.309	12.34	2.52	8.59	4.87
25	1193	50.11	1.55	0.0180	0.971	0.254	0.20	9.33	2.81	6.78	3.84
26	1199	35.45	2.30	0.0537	1.30	0.579	0.382	12.45	2.60	8.36	4.56
27	1203	38.21	1.67	0.0436	1.27	0.602	0.406	13.29	2.46	7.68	4.48
28	1205	30.91	3.13	0.0863	1.32	0.643	0.408	11.83	2.98	7.59	4.18
29	1225	24.21	3.01	0.0796	1.59	0.767	0.529	17.45	2.96	9.36	5.70
30	1235	17.09	3.53	0.108	1.72	0.927	0.631	19.07	2.86	9.19	5.08
31	1250	12.98	5.22	0.20	2.07	1.49	0.917	22.89	3.09	9.01	5.60

The balance of nitrogen vs carbon among the decomposition products is shown in Figure 4. The sum of the concentrations of all of the nitrogen containing products, except for the two isomers of picoline, are plotted against one-sixth the sum of the concentrations of all of the products, each multiplied by the number of its carbon atoms. Including the two picolines, which have the same N/C ratio as the reactant 2,4-dimethylpyrrole, in the mass balance evaluation would underestimate the deviation from a perfect mass balance owing to their high concentration. The diagonal in the figure represents a perfect mass balance. As can be seen, mass balance is maintained in the experiments.

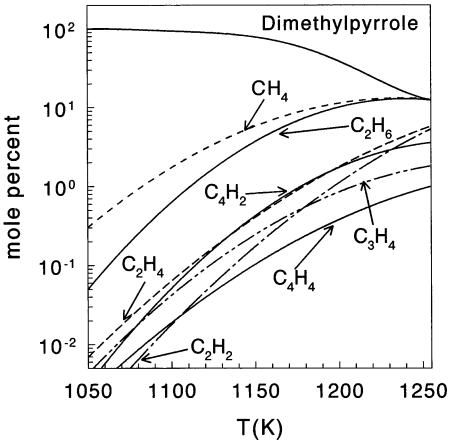


Figure 2. Distribution of reaction products without nitrogen as a function of temperature.

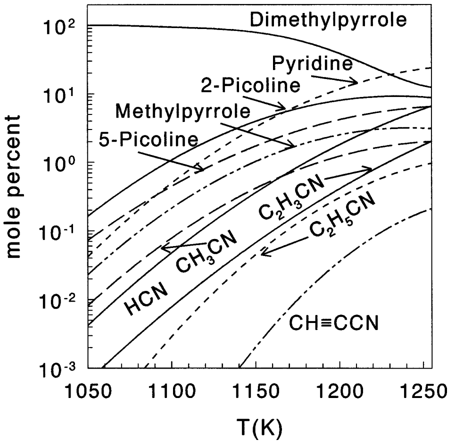


Figure 3. Distribution of reaction products with nitrogen as a function of temperature.

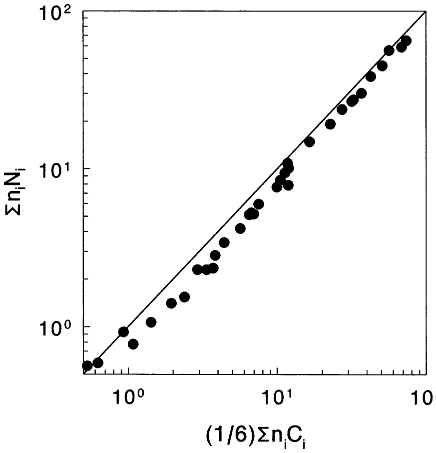


Figure 4. Nitrogen−carbonmass balance among the decomposition products. The 45° line corresponds to a perfect mass balance. Nitrogen−carbon mass balance is maintained.

Figure 5 shows the rate constant for the overall decompositions of 2,4-dimethylpyrrole, calculated as a first-order rate constant from the relation

$$k_{\text{total}} = -\ln\{[\text{2,4-dimethylpyrrole}]_t/[\text{2,4-dimethylpyrrole}]_0\}/t \qquad \text{(VI)}$$

The value obtained is $k_{\text{total}} = 10^{16.31}\exp(-75.7 \times 10^3/RT)\ \text{s}^{-1}$, where R is expressed in units of cal/(K mol). Figures 6 and 7 show Arrhenius plots of the first-order production rate of several products, calculated from the relation

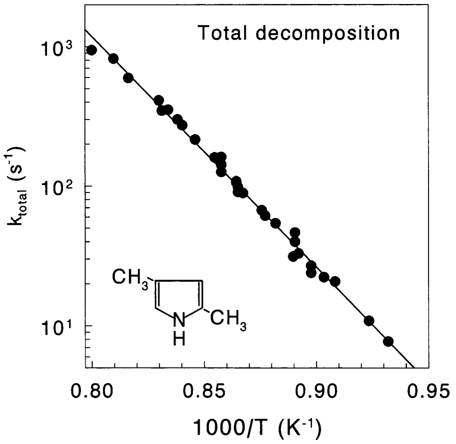


Figure 5. Arrhenius plot of a first-order rate constant for the total decomposition of 2,4-dimethylpyrrole. The value obtained is $k_{\text{total}} = 10^{16.31}\exp(-75.7 \times 10^3/RT)\ \text{s}^{-1}$. See eq VI.

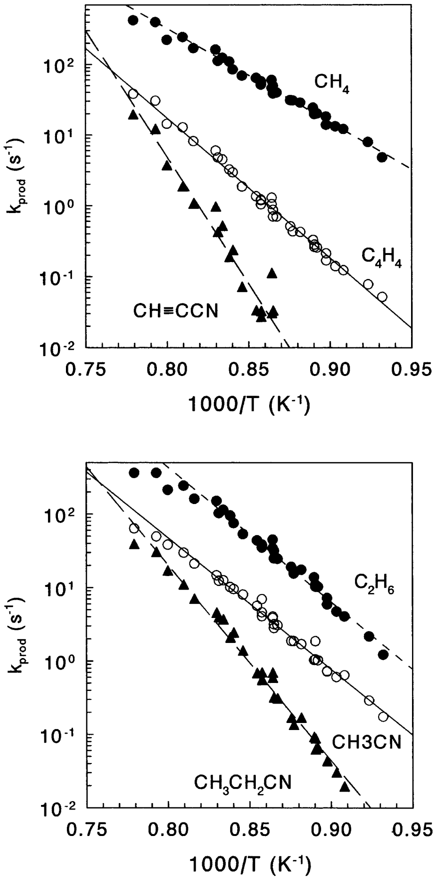


Figure 6. Arrhenius plot for the production of various reaction products. See eq VII and Table 2.

$$k_{\text{product}} = \frac{[\text{product}]_t}{[\text{2,4-dimethyl pyrrole}]_0 - [\text{2,4-dimethyl pyrrole}]_t}\,k_{\text{total}} \qquad \text{(VII)}$$

Note that the values calculated from eq VII correspond to the production rates and not to the depletion rate of the reactant due to the production of a given product. Values of E obtained from the slopes of the lines and their corresponding preexponential factors are summarized in Table 2. Because the production of all of the stable products are associated in one way or

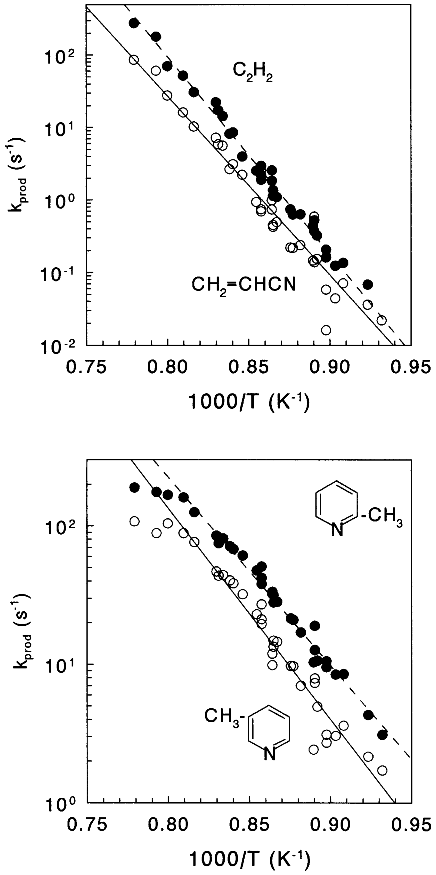
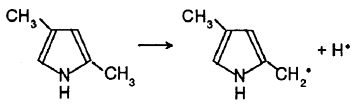


Figure 7. Arrhenius plot for the production of various reaction products. See eq VII and Table 2.

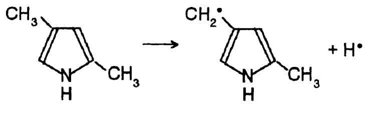
another with free radical reactions, their Arrhenius parameters do not correspond to the parameters of true first-order rate constants. They do provide, however, a convenient way to summarize general rates.

IV. Discussion

A. Initial Production of Free Radicals, Abstractions, and Dissociative Recombinations. The initiation steps that produce free radicals in the decomposition of 2,4-dimethylpyrrole are ejections of hydrogen atoms from the two methyl groups (sp^3 carbons) and dissociation of methyl groups from the pyrrole ring:



(1)



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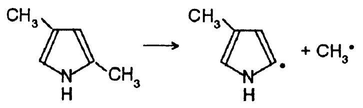

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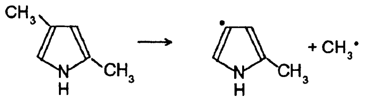


(4)

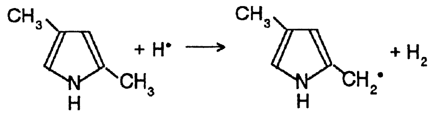
TABLE 2: First Order Arrhenius Parameters for the Production Rates of the Various Reaction Products

no.	products	log *A* (s^{-1})	*E* (kcal/mol)
1	total decomposition	16.31	75.7
2	CH_4	13.18	61.0
3	C_2H_4	19.36	99.4
4	C_2H_6	17.31	83.9
5	C_2H_2	23.78	124.6
6	C_3H_4	17.52	91.0
7	C_4H_2	19.73	101.3
8	C_4H_4	17.09	90.6
9	HCN	20.83	107.5
10	CH≡CCN	29.66	165.5
11	CH_3CN	16.02	82.0
12	C_2H_3CN	21.20	113.0
13	C_2H_5CN	23.61	127.0
14	methylpyrrole	14.82	73.7
15	2-picoline	13.25	62.3
16	5-picoline	14.34	69.8
17	pyridine	18.99	92.9

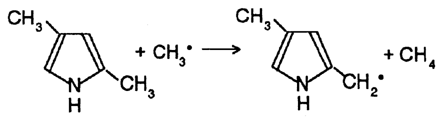
Once the two isomers of methyl pyrrolyl are formed (reactions 3 and 4), they can either undergo ring expansion to yield pyridine or recombine with hydrogen atoms to yield methylpyrrole. The latter depends on the H-atom concentration in the system.

Reactions 3 and 4 are considerably faster than reactions 1−2 having lower activation energies and higher preexponential factors. The removal of a hydrogen atom from the nitrogen is a slow process both statistically (a factor of 6 less probable) and owing to the existence of resonance structures that increase the N−H bond strength. This bond strength increase is due to the fact that in some of the resonance structures the N−H bond has a vinyl type character and is this a stronger bond. This step was neglected in our discussion and computer simulations. Also, the ejection of a hydrogen atom from a sp^2 carbon in the ring is very slow and does not contribute at all to the initial production of hydrogen atoms.

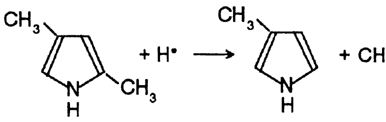
The H atoms and methyl radicals initiate a chain mechanism by abstraction of H atoms from the methyl group and by dissociative recombination of H atoms and removal of methyl groups from the ring. In view of the existence of two methyl groups in the molecule, each of the following reactions is two elementary steps:



(5,6)



(7,8)



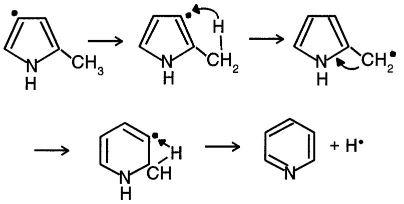
(9,10)

In each one of these reactions, in addition to the methyl radicals and hydrogen atoms that are formed, the remaining unstable intermediates undergo ring cleavage, ring expansion and other processes.

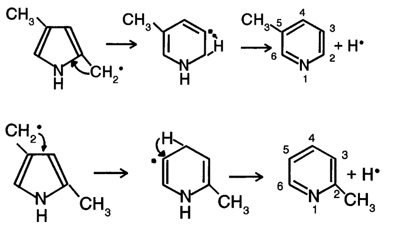
B. Ring Expansion. *a. Introductory Remarks.* As can be seen in the product distribution (Figure 3), the products of ring expansion are among the products of the highest concentration. It has also been shown in the study on the decomposition of *N*-methylpyrrole[8] that ring expansion toward the formation of pyridine is one of the major processes in its thermal reactions. It was assumed that ring expansion takes place from methylene pyrrole radicals rather than from methyl pyrrole itself. In the expansion process, the hydropyridyl radical is formed, and by a fast ejection of a hydrogen atom ($\Delta H \sim 23$ kcal/mol) that follows, pyridine is obtained. This assumption was later verified by detailed quantum chemical calculations for ring expansion from *N*-methylene and 2 and 3-methylene pyrrole.[7] On the other hand, the first transition state on the potential energy surface of the ring expansion process, when *N*-methylpyrrole is the starting molecule, lies about 140 kcal/mol above the energy level of *N*-methylpyrrole.[7] In the transition state, in addition to N−C bond breaking, one of the hydrogen atoms originating from the methyl group is already far removed from its original site on the carbon atom to a distance of 2.35 Å. This means that the energy level of the transition state is determined by both H-atom ejection and N−C bond cleavage.[7] We have assumed that here too, the ring expansion process takes place from methylene methyl pyrrole rather than dimethylpyrrole itself.

There are three possible ring expansion processes in 2,4-dimethylpyrrole. Two processes produce two isomers of picoline (methyl pyridine), 2-picoline, and 5-picoline. One process yields pyridine. All of the three reactions take place from radical species. The two picoline isomers are formed from methylene methylpyrrole. This is a species that is formed after removing a hydrogen atom from a methyl group attached to the ring. Pyridine is formed from a species that is formed after the removal of a methyl group from the molecule.

b. Mechanism. The ring expansion mechanism is based on insertion of a methylene group into a C−C or a C−N bond in the pyrrole ring. It can be expressed schematically as



in methylene methylpyrrole, and as



in methyl pyrrolyl and in methylene pyrrole.

Each methylene group in methylene methylpyrrole can, in principle, be inserted into two different locations in the ring, but the final products of the ring expansion are the same. However, owing to the presence of double bonds in the molecule that are not in full resonance with the single bonds, the insertion into C−C or C−N single bonds has a lower barrier than the insertion into a C=C double bond.

The only difference between the two radicals that are obtained by removing hydrogen atoms from the methyl groups is in the vicinity of the radical site to the nitrogen atom in the ring. As can be seen in Figure 3, the yield of 2-picoline is somewhat higher than that of 5-picoline, indicating that the insertion of the methylene radical into a C−C bond is somewhat easier that the insertion into a C−N bond.

We have demonstrated in the past that the ring expansion of *N*-methylene pyrrole was much faster than the process in the 2- and the 3-methylene pyrrole isomers, having a barrier of only ∼35 kcal/mol, compared to 61 and 74 kcal/mol for the other two.[7] We have also found (yet unpublished) that the isomerization barrier for the isomerization from the 2 position to the N position is equal to ∼50 kcal/mol. We have therefore concluded that the ring expansion will always take place from *N*-methylene pyrrole, regardless of what is the reacting isomer. From the 2- and 3-methylene pyrrole, this will take place following the isomerization process that is the rate determining step. For this reason, we used an activation energy of 48 kcal/mol for reactions 33 and 34 that can be considered to some extent as global reactions.

C. Free Radical Reactions vs Unimolecular Decompositions. As can be seen in Table 1 and Figure 2, there is a considerable yield of low molecular weight products, both with and without nitrogen. However, a reaction scheme based on free radical reactions alone, where the free radical concentrations are determined by the initiation steps discussed previously, could not account for the yields of almost all of the decomposition products. We thus believe that unimolecular ring cleavage processes that produce unstable intermediates play also an important role in the decomposition mechanism. Unimolecular decompositions can take place from both the reactant itself and from unstable species that are formed after the reactant has lost a methyl group or a hydrogen atom (reactions 1−4 and 5−8). The various unimolecular ring cleavage processes starting from the reactant require much higher activation energies even just owing to thermochemical considerations. In fact, sensitivity analyses show that the reactant dissociation is much less important than its dissociation after losing a hydrogen atom or a methyl group. Only the latter was thus considered in the final kinetic scheme. There are many possible reaction channels for unimolecular cleavage of five membered heterocyclics. We introduced into the kinetic scheme steps that are known in similar systems[14−17] and several assumed channels. A few of these reaction steps are listed in Scheme 1.

It should be mentioned, however, that by no means these reactions should be considered as one concerted step each. They probably involve a series of consecutive reactions that can only be established by quantum chemical calculations. For the purpose of modeling, we have estimated an apparent rate constant for the entire process which is expressed by a simple unimolecular reaction.

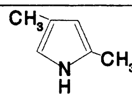
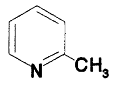
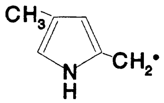
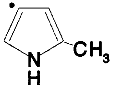
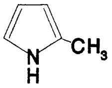
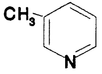
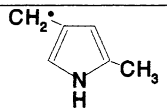
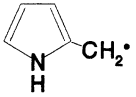
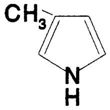
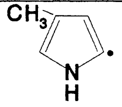
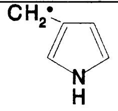
D. Computer Modeling. *a. Reaction Scheme*. To model the observed product distribution, we have constructed the reaction scheme that is shown in Table 3. The scheme contains 36 species and 69 elementary reactions. The symbol (R) at the end of a reaction in the scheme indicates that, after a reaction time of 2 ms (or earlier), the reaction proceeds in the reverse direction. The rate constants listed in the table are given as $k = A \exp(-E/RT)$ or $k = A'T^n \exp(-E/RT)$ when the rate constant taken from the database fits a wide temperature range. The units are cm^3, s^{-1}, kcal, and mol^{-1}. The Arrhenius parameters for the reactions in the scheme are either estimated or taken from various literature sources. These sources are specific articles relevant to the present system and databases, mainly the NIST-Kinetic Standard Reference Data Base 17.[18] The parameters for

TABLE 3: Reaction Scheme for the Decomposition of 2,4-Dimethylpyrrole

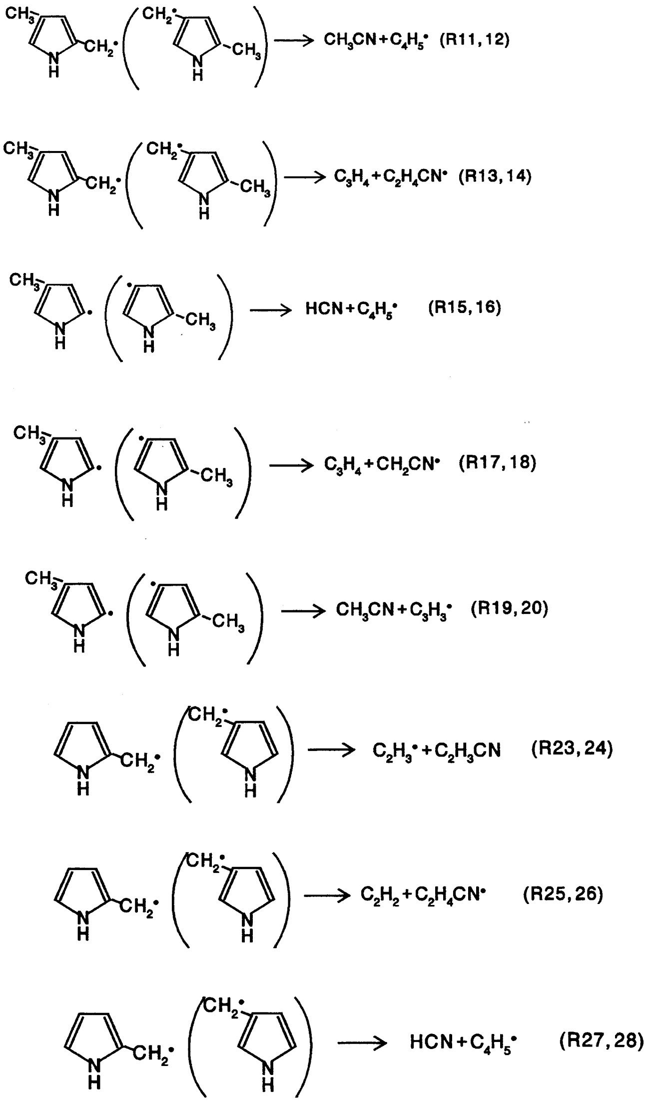
no	reactions	A (s^{-1})	E (kcal/mol)	k_f (1150 K)	k_r (1150 K)	ΔS_r (1150 K)	ΔH_r (1150 K)	ref
1	DMPyrrole → DMPyrrole(R1)$^\bullet$ + $H^\bullet$	3.0×10^{15}	78	4.52	4.64×10^{14}	30.8	83.0	est
2	DMPyrrole → DMPyrrole(R2)$^\bullet$ + $H^\bullet$	3.0×10^{15}	78	4.52	4.64×10^{14}	30.8	83.0	est
3	DMPyrrole → MPyrrole(R1)$^\bullet$ + $CH_3^\bullet$	4.0×10^{16}	80	25.1	3.52×10^{12}	46.7	86.1	est
4	DMPyrrole → MPyrrole(R2)$^\bullet$ + $CH_3^\bullet$	4.0×10^{16}	80	25.1	3.52×10^{12}	46.7	86.1	est
5	DMPyrrole + $H^\bullet$ → DMPyrrole(R1)$^\bullet$ + H_2	1.20×10^{14}	9	2.34×10^{12}	1.38×10^{7}	3.34	−23.7	est
6	DMPyrrole + $H^\bullet$ → DMPyrrole(R2)$^\bullet$ + H_2	1.20×10^{14}	9	2.34×10^{12}	1.38×10^{7}	3.34	−23.7	est
7	DMPyrrole + $CH_3^\bullet$ → DMPyrrole(R1)$^\bullet$ + CH_4	1.0×10^{13}	15	1.41×10^{10}	1.54×10^{6}	−3.40	−24.8	est
8	DMPyrrole + $CH_3^\bullet$ → DMPyrrole(R2)$^\bullet$ + CH_4	1.0×10^{13}	15	1.41×10^{10}	1.54×10^{6}	−3.40	−24.8	est
9	DMPyrrole + $H^\bullet$ → 2-MPyrrole + $CH_3^\bullet$	1.0×10^{14}	8	3.02×10^{12}	6.66×10^{8}	7.23	−10.9	est
10	DMPyrrole + $H^\bullet$ → 4-MPyrrole + $CH_3^\bullet$	1.0×10^{14}	8	3.02×10^{12}	6.66×10^{8}	7.23	−10.9	est
11	DMPyrrole(R1)$^\bullet$ → CH_3CN + $C_4H_5^\bullet$	2.50×10^{13}	68	2.99	4.48×10^{7}	40.6	58.3	est
12	DMPyrrole(R2)$^\bullet$ → CH_3CN + $C_4H_5^\bullet$	2.50×10^{13}	68	2.99	4.48×10^{7}	40.6	58.3	est
13	DMPyrrole(R1)$^\bullet$ → C_3H_4 + $C_2H_4CN^\bullet$	8.0×10^{13}	60	317.0	4.48×10^{7}	44.8	52.4	est
14	DMPyrrole(R2)$^\bullet$ → C_3H_4 + $C_2H_4CN^\bullet$	8.0×10^{13}	60	317.0	4.48×10^{7}	44.8	52.4	est
15	MPyrrole(R1)$^\bullet$ → HCN + $C_4H_5^\bullet$	2.50×10^{13}	60	99.1	1.22×10^{9}	32.1	48.1	est
16	MPyrrole(R2)$^\bullet$ → HCN + $C_4H_5^\bullet$	2.50×10^{13}	60	99.1	1.22×10^{9}	32.1	48.1	est
17	MPyrrole(R1)$^\bullet$ → C_3H_4 + $CH_2CN^\bullet$	2.50×10^{13}	62.5	33.2	1.43×10^{7}	34.3	43.0	est
18	MPyrrole(R2)$^\bullet$ → C_3H_4 + $CH_2CN^\bullet$	2.50×10^{13}	62.5	33.2	1.43×10^{7}	34.3	43.0	est
19	MPyrrole(R1)$^\bullet$ → CH_3CN + $C_3H_3^\bullet$	2.50×10^{13}	60	99.1	4.87×10^{7}	33.2	41.9	est
20	MPyrrole(R2)$^\bullet$ → CH_3CN + $C_3H_3^\bullet$	2.50×10^{13}	60	99.1	4.87×10^{7}	33.2	41.9	est
21	DMPyrrole(R1)$^\bullet$ + $H^\bullet$ → MPyrrole(R3)$^\bullet$ + $CH_3^\bullet$	1.0×10^{14}	7	4.68×10^{12}	8.68×10^{8}	7.54	−11.0	est
22	DMPyrrole(R2)$^\bullet$ + $H^\bullet$ → MPyrrole(R4)$^\bullet$ + $CH_3^\bullet$	1.0×10^{14}	7	4.68×10^{12}	8.68×10^{8}	7.54	−11.0	est
23	MPyrrole(R3)$^\bullet$ → C_2H_3 + C_2H_3CN	2.50×10^{13}	78	0.0376	6.21×10^{6}	44.3	68.1	est
24	MPyrrole(R4)$^\bullet$ → C_2H_3 + C_2H_3CN	2.50×10^{13}	78	0.0376	6.21×10^{6}	44.3	68.1	est
25	MPyrrole(R3)$^\bullet$ → C_2H_2 + $C_2H_4CN^\bullet$	2.50×10^{13}	65	11.1	1.20×10^{7}	43.0	55.1	est
26	MPyrrole(R4)$^\bullet$ → C_2H_2 + $C_2H_4CN^\bullet$	2.50×10^{13}	65	11.1	1.20×10^{7}	43.0	55.1	est
27	MPyrrole(R3)$^\bullet$ → HCN + $C_4H_5^\bullet$	2.50×10^{13}	72	0.520	4.71×10^{7}	40.5	62.2	est
28	MPyrrole(R4)$^\bullet$ → HCN + $C_4H_5^\bullet$	2.50×10^{13}	72	0.520	4.71×10^{7}	40.5	62.2	est
29	DMPyrrole(R1)$^\bullet$ → 5-Picoline + $H^\bullet$	1.62×10^{13}	50.6	3.89×10^{3}	7.34×10^{10}	21.0	36.3	est
30	DMPyrrole(R2)$^\bullet$ → 2-Picoline + $H^\bullet$	6.0×10^{13}	47	7.03×10^{4}	1.32×10^{12}	21.0	36.3	est
31	MPyrrole(R1)$^\bullet$ → Pyridine + $H^\bullet$	1.0×10^{13}	60	39.6	9.67×10^{8}	11.1	25.5	est
32	MPyrrole(R2)$^\bullet$ → Pyridine + $H^\bullet$	1.0×10^{13}	60	39.6	9.67×10^{8}	11.1	25.5	est
33	MPyrrole(R3)$^\bullet$ → Pyridine + $H^\bullet$	5.0×10^{13}	48	3.78×10^{4}	6.78×10^{12}	19.4	39.6	7, mod.
34	MPyrrole(R4)$^\bullet$ → Pyridine + $H^\bullet$	5.0×10^{13}	48	3.78×10^{4}	6.78×10^{12}	19.4	39.6	7, mod.
35	2-Picoline + $H^\bullet$ → Pyridine + $CH_3^\bullet$	2.0×10^{14}	7	9.35×10^{12}	1.65×10^{10}	5.96	−7.64	est
36	5-Picoline + $H^\bullet$ → Pyridine + $CH_3^\bullet$	2.0×10^{14}	7	9.35×10^{12}	1.65×10^{10}	5.96	−7.64	est
37	MPyrrole(R1)$^\bullet$ + $H^\bullet$ → 4-MPyrrole	1.0×10^{14}	0	1.0×10^{14}	0.157	−39.4	−97.1	est
38	MPyrrole(R2)$^\bullet$ + $H^\bullet$ → 2-MPyrrole	1.0×10^{14}	0	1.0×10^{14}	0.157	−39.4	−97.1	est
39	MPyrrole(R3)$^\bullet$ + $H^\bullet$ → 2-MPyrrole	1.0×10^{14}	0	1.0×10^{14}	1.16	−31.1	−82.9	est
40	MPyrrole(R4)$^\bullet$ + $H^\bullet$ → 4-MPyrrole	1.0×10^{14}	0	1.0×10^{14}	1.16	−31.1	−82.9	est
41	2-MPyrrole + $H^\bullet$ → MPyrrole(R3)$^\bullet$ + H_2	3.0×10^{14}	10	3.77×10^{12}	1.87×10^{7}	3.65	−23.7	est
42	4-MPyrrole + $H^\bullet$ → MPyrrole(R4)$^\bullet$ + H_2	3.0×10^{14}	10	3.77×10^{12}	1.87×10^{7}	3.65	−23.7	est
43	2-MPyrrole + $CH_3^\bullet$ → MPyrrole(R3)$^\bullet$ + CH_4	5.0×10^{13}	8	1.51×10^{12}	1.39×10^{8}	−3.09	−24.8	8, mod.
44	4-MPyrrole + $CH_3^\bullet$ → MPyrrole(R4)$^\bullet$ + CH_4	5.0×10^{13}	8	1.51×10^{12}	1.39×10^{8}	−3.09	−24.8	8, mod.
45	$C_4H_5^\bullet \rightarrow C_4H_4 + H^\bullet$	5.0×10^{13}	51	1.02×10^{4}	1.40×10^{12}	29.7	50.8	18, mod.
46	$C_4H_5^\bullet + H^\bullet \rightarrow C_4H_6$	1.0×10^{14}	0	1.0×10^{14}	1.60×10^{-2}	−30.4	−91.9	est
47	$C_4H_3^\bullet + H^\bullet \rightarrow C_4H_4$	3.0×10^{14}	0	3.0×10^{14}	$2. \times 10^{-4}$	−33.0	−107.4	18, mod.
48	$C_4H_3^\bullet \rightarrow C_4H_2 + H^\bullet$	7.96×10^{13}	34	2.75×10^{7}	3.53×10^{13}	24.2	33.7	18
49	$C_4H_4 + H^\bullet \rightarrow C_4H_3^\bullet + H_2$	5.0×10^{14}	9	9.74×10^{12}	8.14×10^{11}	5.57	0.727	29, mod.
50	$C_2H_6 + H^\bullet \rightarrow C_2H_5^\bullet + H_2$	1.43×10^{14}	9.56	2.18×10^{12}	5.21×10^{9}	8.18	−4.39	18
51	$C_4H_4 + H^\bullet \rightarrow C_2H_2 + C_2H_3^\bullet$	5.0×10^{14}	7	2.34×10^{13}	3.78×10^{11}	6.79	−1.63	est
52	$C_3H_4 + H^\bullet \rightarrow CH_3^\bullet + C_2H_2$	5.0×10^{14}	7	2.34×10^{13}	3.32×10^{10}	5.82	−8.30	18, mod.
53	$C_2H_6 + CH_3^\bullet \rightarrow C_2H_5^\bullet + CH_4$	$1.64T^{4}$	8.29	7.64×10^{10}	3.39×10^{9}	1.44	−5.47	24
54	$CH_4 + Ar \rightarrow CH_3^\bullet + H^\bullet + Ar$(R)	1.50×10^{17}	88.6	2.24	2.10×10^{18}	34.2	107.7	21
55	$CH_4 + H^\bullet \rightarrow CH_3^\bullet + H_2$(R)	1.44×10^{14}	12.3	6.75×10^{11}	3.63×10^{10}	6.74	1.07	18
56	$CH_3^\bullet + CH_3^\bullet \rightarrow C_2H_6$	$1.01 \times 10^{15}T^{-0.64}$	0	1.11×10^{13}	4.62×10^{-1}	−40.4	−90.7	26
57	$CH_3^\bullet + CH_3^\bullet \rightarrow C_2H_5^\bullet + H^\bullet$	3.01×10^{13}	13.5	8.14×10^{10}	1.41×10^{14}	−4.80	11.5	26
58	$CH_3^\bullet + CH_3^\bullet \rightarrow C_2H_4 + H_2$	4.72×10^{15}	30.8	6.59×10^{9}	4.44	−7.55	−57.0	18
59	$C_2H_5^\bullet \rightarrow C_2H_4 + H^\bullet$	$4.80 \times 10^{9}T^{1.19}$	37.2	1.79×10^{6}	1.21×10^{13}	24.7	38.2	24
60	$C_2H_3^\bullet \rightarrow C_2H_2 + H^\bullet$	2.0×10^{14}	39.7	5.71×10^{6}	4.26×10^{13}	23.7	37.3	26
61	$CH_3CN \rightarrow CH_2CN^\bullet + H^\bullet$(R)	1.00×10^{15}	93	2.12×10^{-3}	5.20×10^{12}	34.1	94.0	28
62	$CH_3CN + H^\bullet \rightarrow CH_3^\bullet + HCN$	1.0×10^{14}	7	4.68×10^{12}	5.26×10^{9}	7.35	−7.06	27, mod.
63	$CH_3CN + CH_3^\bullet \rightarrow CH_4 + CH_2CN^\bullet$	3.0×10^{12}	12	1.57×10^{10}	4.10×10^{7}	−0.089	−13.7	28
64	$CH_3CN + H^\bullet \rightarrow H_2 + CH_2CN^\bullet$	2.0×10^{14}	7	9.35×10^{12}	1.31×10^{9}	6.65	−12.6	28
65	$CH_2CN^\bullet + CH_3^\bullet \rightarrow C_2H_5CN$	3.0×10^{12}	0	3.0×10^{12}	1.70	−39.5	−83.7	27, mod.
66	$C_2H_5CN + H^\bullet \rightarrow C_2H_4CN^\bullet + H_2$	5.0×10^{14}	7	2.34×10^{13}	5.67×10^{8}	6.65	−16.6	28, mod.
67	$C_2H_4CN \rightarrow C_2H_3CN + H^\bullet$	3.0×10^{13}	50	9.45×10^{3}	1.07×10^{13}	25.0	50.2	28, mod.
68	$C_2H_3CN + H^\bullet \rightarrow H_2 + CH{=}CHCN^\bullet$	5.0×10^{14}	9	9.74×10^{12}	2.24×10^{12}	3.68	0.870	28, mod.
69	$CH{=}CHCN^\bullet \rightarrow CH{\equiv}CCN + H^\bullet$	1.0×10^{13}	40	2.50×10^{5}	2.27×10^{14}	23.8	48.3	28

TABLE 3 (Continued)

Glossary

DMPyrrole: 	2-Picoline: 	DMPyrrole(R1)•: 	MPyrrole(R2)•: 
2-Mpyrrole: 	5-Picoline: 	DMPyrrole(R2)•: 	MPyrrole(R3)•: 
4-Mpyrrole: 	C_3H_4: $CH_3\text{-}C{\equiv}CH + CH_2{=}C{=}CH_2$	MPyrrole(R1)•: 	MPyrrole(R4)•: 

SCHEME 1



the reactions that were taken from the NIST-Kinetics Data Base are, in many cases, best fits to a large number of entries. The thermodynamic properties of the species in the scheme were also taken from specific articles and various literature sources.[19−21] Some were estimated using NIST−Standard Reference Data Base 25[22] (Structure and Properties program (SP)).

Figure 8 shows the overall decomposition of 2,4-dimethylpyrrole and Figures 9−14 show experimental and calculated yields of sixteen products found in the post-shock mixtures. The symbols in the figures are the experimental yields in mole percent, and the lines are the best fits to the calculated points using the scheme shown in Table 3. The calculations were done at 25 K intervals in the temperature range 1050−1250 and are shown as (+) on the lines. The agreement between the model

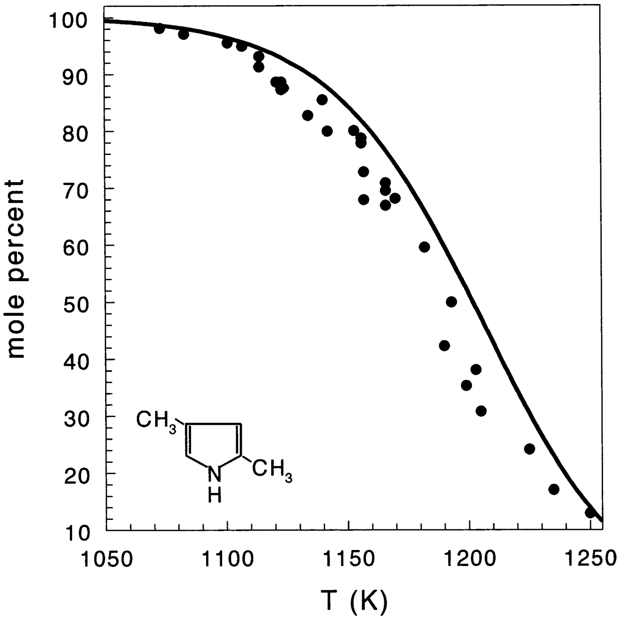


Figure 8. Calculated and experimental mole percent of 2,4-dimethylpyrrole left after shock heating as a function of temperature. The calculations are done at 25 K intervals.

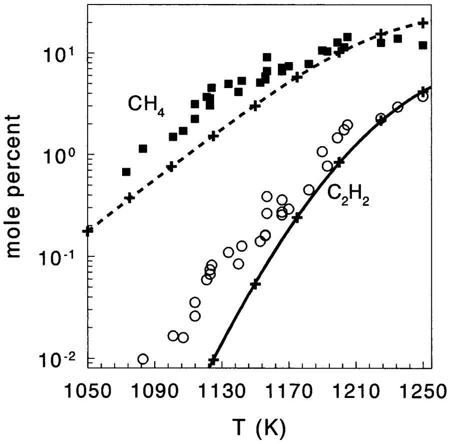


Figure 9. Calculated (lines) and experimental yields of methane and acetylene. The calculations are done at 25 K interval, marked on the lines as crosses.

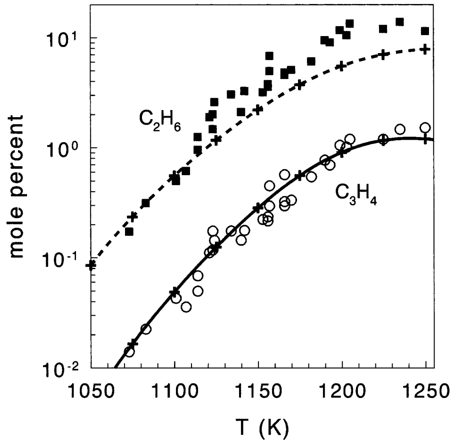


Figure 10. Calculated (lines) and experimental yields of ethane and C_3H_4 (allene and methylacetylene). The calculations are done at 25 K interval, marked on the lines as crosses.

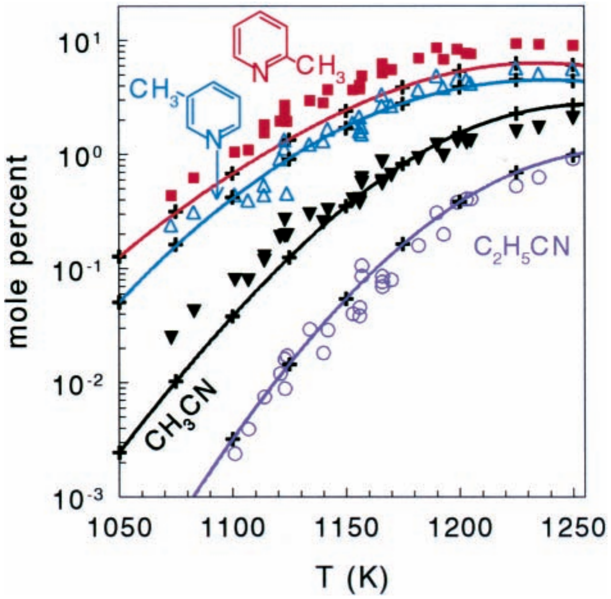


Figure 11. Calculated (lines) and experimental yields of 2-picoline, 4-picoline, acetonitrile, and propylnitrile. The calculations are done at 25 K interval, marked on the lines as crosses.

prediction and the experimental results is satisfactory for most of the products but not very good for C_2H_4, C_4H_4, C_4H_2, and methylpyrrole. The model underestimates the yield of C_4H_2 and overestimates somewhat the yield of C_4H_4. We could not suggest a route where some of the C_4H_4 yield is transferred to C_4H_2 unless a major change in the available rate constant had to be made.

Note the symbol (R) at the end of reaction 1 in the kinetic scheme, which indicates that the reaction proceeds in the reverse direction, whereas reaction 2 proceeds all the way in the forward direction. Reversal in the direction of reaction 1 begins after approximately 920 out of a reaction time of 2000 μs. The reason for this behavior is the different production rates of the two isomers of picoline via reactions 29 and 30 (Table 3) from the unstable species that are formed in reactions 1 and 2. As can be seen in Figure 11, the yields of the two picoline isomers are high and the yield of 2-picoline is higher that that of 5-picoline. We have assigned a higher rate constant to reaction 30 that produces 2-picoline by lowering its activation energy by approximately 3.5 kcal/mol. The high rate of reaction 30 produces high enough yield of hydrogen atoms to change the direction of reaction 1 after some 900 μs.

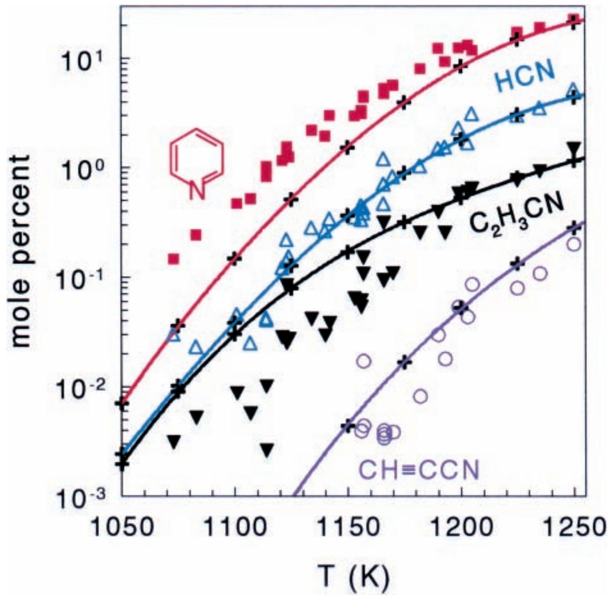


Figure 12. Calculated (lines) and experimental yields of pyridine, hydrogen cyanide, acrilonitrile, and cyanoacetylene. The calculations are done at 25 K interval, marked on the lines as crosses.

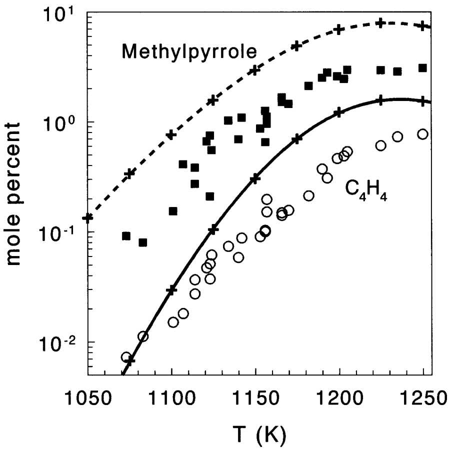


Figure 13. Calculated (lines) and experimental yields of methylpyrrole (two isomers), and C_4H_4. The calculations are done at 25 K interval, marked on the lines as crosses.

b. Sensitivity Analysis. Table 4 shows the sensitivity of the products to elimination of specific reactions from the kinetic scheme, at 1100 and 1200 K, respectively. It gives the percent change in the yield of a particular product as a result of eliminating a given reaction from the scheme. The calculations correspond to dwell times of 2 ms. Reactions that show an effect of less than 10% both at 1100 and at 1200 K are not included in the table. As can be seen in Table 3, there are several pairs of reactions where two similar radical species produce the same products. Elimination of only one reaction out of the two has much weaker effect than the eliminating the pair of reactions.

We have run also sensitivity analysis with respect to variations (or rather uncertainties) in the $\Delta_f H^0$ of species whose thermodynamic properties were estimated or are not known very accurately. Incorrect values of the thermodynamic functions result in erroneous values for the rate constants of the back reactions for a given value of the forward rate constant. In several sensitivity tests that were performed on uncertain values of heat of formation of various species, we found that the results of the computer simulations were only slightly sensitive to variations of ~3 kcal/mol in the values of the estimated $\Delta_f H^0$.

TABLE 4: Sensitivity Spectrum at 1100/1200 K[a]

A. Products with Nitrogen

no.	reactions	2-MPyrrole	4-MPyrrole	2-picoline	5-picoline	pyridine	HCN	CH≡CCN	CH_3CN	C_2H_3CN	C_2H_5CN
1	DMPyrrole → DMPyrrole(R1) + $H^{\bullet}$	−12/−	−12/−	−/−	−20/−	−17/−	−/−	−28/−13	−/−	−18/−	−/−
2	DMPyrrole → DMPyrrole(R2) + $H^{\bullet}$	−25/−13	−25/−13	−32/−34	−/−	−30/−18	−/−	−36/−27	−/13	−15/−	−/10
3	DMPyrrole → MPyrrole(R1) + $CH_3^{\bullet}$	−/19	−15/−42	−11/−	−11/−	−30/−20	−48/−43	−18/−	−48/−43	−11/−	−57/−47
4	DMPyrrole → MPyrrole(R2) + $CH_3^{\bullet}$	−15/−42	−/19	−11/−	−11/−	−30/−20	−48/−43	−18/−	−48/−43	−11/−	−57/−47
5	DMPyrrole + $H^{\bullet}$ → DMPyrrole(R1) + H2	18/13	18/13	−/−	−36/−36	21/12	−/−	− /−15	−/−	−25/−28	−/−
6	DMPyrrole + H → DMPyrrole(R2) + H_2	−/−	−/−	−37/−45	−/−	−/−	−/−	−/−	−/−	−/−	−/−
7	DMPyrrole + $CH_3^{\bullet}$ → DMPyrrole(R1) + CH_4	−/−	−/−	−/−	−41/−20	−/−	−/−	−35/−16	−/−	−30/−13	−/−
8	DMPyrrole + $CH_3^{\bullet}$ → DMPyrrole(R2) + CH_4	−20/−	−20/−	−45/−21	−/−	−15/−	−/−	−30/−	−/−	−12/−	−/−
9	DMPyrrole + $H^{\bullet}$ → 2-MPyrrole + $CH_3^{\bullet}$	−82/−43	33/11	−/−	−/−	−23/−14	−/−	37/12	−/−	−/−	−/−
10	DMPyrrole + H → 4-MPyrrole + $CH_3^{\bullet}$	33/11	−82/−43	−/−	−/−	−23/−14	−/−	37/12	−/−	−/−	−/−
13	DMPyrrole(R1) → C_3H_4 + $C_2H_4CN^{\bullet}$	−/−	−/−	−/−	−/−	−/−	−/−	−73/−70	−/−	−75/−65	−/−
14	DMPyrrole(R2) → C_3H_4 + $C_2H_4CN^{\bullet}$	−/−	−/−	−/−	−/−	−/−	−/−	−26/−21	−/−	−24/−19	−/−
15	MPyrrole(R1) → HCN + $C_4H_5^{\bullet}$	−/−	−/−	−/−	−/−	−/−	−49/−46	−/−	−/11	−/−	−/−
16	MPyrrole(R2) → HCN + $C_4H_5^{\bullet}$	−/−	−/−	−/−	−/−	−/−	−49/−46	−/−	−/11	−/−	−/−
17	MPyrrole(R1) → C_3H_4 + $CH_2CN^{\bullet}$	−/−	−/−	−/−	−/−	−/−	−/−	−/−	−/−	−/−	−49/−41
18	MPyrrole(R2) → C_3H_4 + $CH_2CN^{\bullet}$	−/−	−/−	−/−	−/−	−/−	−/−	−/−	−/−	−/−	−49/−41
19	MPyrrole(R1) → CH_3CN + $C_3H_3^{\bullet}$	−/−	−/−	−/−	−/−	−/−	−/−	−/−	−49/−48	−/−	−/−
20	MPyrrole(R2) → CH_3CN + $C_3H_3^{\bullet}$	−/−	−/−	−/−	−/−	−/−	−/−	−/−	−49/−48	−/−	−/−
29	DMPyrrole(R1) → 5-Picoline + $H^{\bullet}$	−35/−27	−35/−27	−13/−	−99/−98	−32/−30	−/13	−21/47	−/21	45/138	−/14
30	DMPyrrole(R2) → 2-Picoline + $H^{\bullet}$	−50/−34	−50/−34	−99/−99	−15/−	−50/−37	−/16	−23/60	−/26	79/191	−/18
33	MPyrrole(R3) → Pyridine + $H^{\bullet}$	−/−	−/−24	−/−	−/−	−45/−51	−/−	−/−30	−/14	−/−	−/−
34	MPyrrole(R4) → Pyridine + $H^{\bullet}$	−/−23	−/−	−/−	−/−	−44/−51	−/−	−/−30	−/14	−/−	−/−
37	MPyrrole(R1) + $H^{\bullet}$ → 4-MPyrrole	−/−	−/−45	−/−	−/−	−/−	−/18	−/22	−/15	−/−	−/17
38	MPyrrole(R2) + $H^{\bullet}$ → 2-MPyrrole	−/−45	−/−	−/−	−/−	−/−	−/18	−/22	−/15	−/−	−/17
43	2-MPyrrole + $CH_3^{\bullet}$ → MPyrrole(R3) + CH_4	13/72	−/−21	−/−	−/−	−42/−42	−/−	−/−19	−/−	−/−	−/12
44	4-MPyrrole + $CH_3^{\bullet}$ → MPyrrole(R4) + CH_4	−/−21	13/72	−/−	−/−	−42/−42	−/−	−/−19	−/−	−/−	−/12
45	$C_4H_5^{\bullet}$ → C_4H_4 + $H^{\bullet}$	−/−16	−/−16	−/−	−/−	−/−13	−/−	−/−23	−/10	−/−	−/−
56	$CH_3^{\bullet}$ + $CH_3^{\bullet}$ → C_2H_6	13/−45	13/−45	61/46	49/36	167/ 79	−/−25	117/102	−/−31	48/38	85/−
65	$CH_2CN^{\bullet}$ + $CH_3^{\bullet}$ → C_2H_5CN	−/−	−/−	−/−	−/−	−/−	−/−	−/−	−/−	−/−14	−99/−99
66	C_2H_5CN + $H^{\bullet}$ → $C_2H_4CN^{\bullet}$ + H_2	−/−	−/−	−/−	−/−	−/−	−/−	−/−	−/−	−/−14	−/18
67	C_2H_4CN → C_2H_3CN + $H^{\bullet}$	−/−	−/−	−/−	−/−	−/−	−/−	−99/−99	−/−	−99/−99	−/−
68	C_2H_3CN + $H^{\bullet}$ → H_2 + CH═CHCN$^{\bullet}$	−/−	−/−	−/−	−/−	−/−	−/−	−100/−100	−/−	−/−	−/−
69	CH═CHCN$^{\bullet}$ → CH≡CCN + $H^{\bullet}$	−/−	−/−	−/−	−/−	−/−	−/−	−100/−100	−/−	−/−	−/−

B. Products without Nitrogen

no.	reactions	CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_4	C_4H_6	C_4H_2	C_4H_4
1	DMPyrrole → DMPyrrole(R1) + $H^{\bullet}$	-/-	-/-	-/-	−15/−	−12/−	-/-	-/-	-/-
2	DMPyrrole → DMPyrrole(R2) + $H^{\bullet}$	−10/−13	−14/−	-/-	−27/−11	−10/−	−22/−12	−21/−	-/18
3	DMPyrrole → MPyrrole(R1) + $CH_3^{\bullet}$	−25/−19	−49/−37	−41/−29	−38/−36	−20/−23	−52/−43	−52/−42	−48/−43
4	DMPyrrole → MPyrrole(R2) + $CH_3^{\bullet}$	−25/−19	−49/−37	−41/−29	−38/36	−20/−23	−52/−43	−52/−42	−48/−43
5	DMPyrrole + $H^{\bullet}$ → DMPyrrole(R1) + H2	-/10	-/-	-/-	-/-	−20/−19	16/11	16/10	-/-
7	DMPyrrole + $CH_3^{\bullet}$ → DMPyrrole(R1) + CH_4	−35/−10	21/−	16/−	−18/−	−23/−	-/-	-/-	-/-
8	DMPyrrole + $CH_3^{\bullet}$ → DMPyrrole(R2) + CH_4	−39/−12	13/−	12/−	−22/−	-/-	−18/−	−18/−	-/-
9	DMPyrrole + $H^{\bullet}$ → 2-MPyrrole + $CH_3^{\bullet}$	−10/−13	−13/−	−13/−	29/−	-/-	27/−	26/−	-/-
10	DMPyrrole + H → 4-MPyrrole + $CH_3^{\bullet}$	−10/−13	−13/−	−13/−	29/−	-/	−27/−	26/−	-/-
13	DMPyrrole(R1) → C_3H_4 + $C_2H_4CN^{\bullet}$	-/-	-/-	-/-	−29/−	−57/−29	-/-	-/-	-/-
14	DMPyrrole(R2) → C_3H_4 + $C_2H_4CN^{\bullet}$	-/-	-/-	-/-	-/-	−17/−	-/-	-/-	-/-
15	MPyrrole(R1) → HCN + $C_4H_5^{\bullet}$	-/-	-/-	-/-	−25/−39	-/-	−50/−52	−50/−52	−49/−46
16	MPyrrole(R2) → HCN + $C_4H_5^{\bullet}$	-/-	-/-	-/-	−25/−39	-/-	−50/−52	−50/−52	−49/−46
17	MPyrrole(R1) → C_3H_4 + $CH_2CN^{\bullet}$	-/-	-/-	-/-	-/-	−12/−29	-/-	-/-	-/-
18	MPyrrole(R2) → C_3H_4 + $CH_2CN^{\bullet}$	-/-	-/-	-/-	-/-	−12/−29	-/-	-/-	-/-
29	DMPyrrole(R1) → 5-Picoline + $H^{\bullet}$	−12/−21	−18/−14	−12/−	−31/−14	40/88	−37/−25	−39/−23/	-/30
30	DMPyrrole(R2) → 2-Picoline + $H^{\bullet}$	−19/−27	−26/−17	−18/−	−39/−18	67/120	−50/−31	−50/−29	-/38
33	MPyrrole(R3) → Pyridine + $H^{\bullet}$	-/−12	-/−14	-/-	-/−20	-/11	-/−21	-/−26	-/22
34	MPyrrole(R4) → Pyridine + $H^{\bullet}$	-/−11	-/−14	-/-	-/−20	-/11	-/−21	-/−26	-/22
37	MPyrrole(R1) + $H^{\bullet}$ → 4-MPyrrole	-/-	-/14	-/-	-/30	-/-	-/43	-/31	-/11
38	MPyrrole(R2) + $H^{\bullet}$ → 2-MPyrrole	-/-	-/14	-/-	-/30	-/-	-/43	-/31	-/11
43	2-MPyrrole + $CH_3^{\bullet}$ → MPyrrole(R3) + CH_4	-/−32	-/11	-/15	-/−15	-/-	-/−12	-/−14	-/13
44	4-MPyrrole + $CH_3^{\bullet}$ → MPyrrole(R4) + CH_4	-/−32	-/11	-/15	-/−15	-/-	-/−12	-/−14	-/13
45	$C_4H_5^{\bullet}$ → C_4H_4 + $H^{\bullet}$	-/−10	-/-	-/-	−50/−78	-/-	214/1107	−100/−100	−100/−99
46	$C_4H_5^{\bullet}$ + $H^{\bullet}$ → C_4H_6	-/-	-/-	-/-	-/-	-/-	−100/−100	-/-	-/-
48	$C_4H_3^{\bullet}$ → C_4H_2 + $H^{\bullet}$	-/-	-/-	-/-	-/-	-/-	-/-	−99/−99	-/-
49	C_4H_4 + $H^{\bullet}$ → $C_4H_3^{\bullet}$ + H_2	-/-	-/-	-/-	-/-	-/-	-/-	−99/−99	-/-
50	C_2H_6 + $H^{\bullet}$ → $C_2H_5^{\bullet}$ + H_2	-/-	-/−26	-/-	-/-	-/-	-/-	-/-	-/-
51	C_4H_4 + $H^{\bullet}$ → C_2H_2 + $C_2H_3^{\bullet}$	-/-	-/-	-/-	−48/−73	-/-	-/-	-/14	-/22
52	C_3H_4 + $H^{\bullet}$ → $CH_3^{\bullet}$ + C_2H_2	-/-	-/-	-/-	−49/−24	-/24	-/-	-/-	-/-
53	C_2H_6 + $CH_3^{\bullet}$ → $C_2H_5^{\bullet}$ + CH_4	-/-	-/−61	-/-	-/-	-/-	-/-	-/-	-/-
56	$CH_3^{\bullet}$ + $CH_3^{\bullet}$ → C_2H_6	145/123	120/−	−99/−99	79/12	37/−	44/10	50/−	−/−37
57	$CH_3^{\bullet}$ + $CH_3^{\bullet}$ → $C_2H_5^{\bullet}$ + $H^{\bullet}$	-/-	−35/−	-/-	-/-	-/-	-/-	-/-	-/-
59	$C_2H_5^{\bullet}$ → C_2H_4 + $H^{\bullet}$	-/-	−97/−98	-/-	-/-	-/-	-/-	-/-	-/-
60	$C_2H_3^{\bullet}$ → C_2H_2 + $H^{\bullet}$	-/-	-/-	-/-	−24/−41	-/-	-/-	-/-	-/-

[a] Percent change in the yields for elimination of a reaction from the scheme. (A) Products with nitrogen and (B) products without nitrogen.

As expected, not all of the elementary steps affect the product distribution in the sense that their elimination from the scheme affects the yield of at least one of the products. The majority of the steps that compose the scheme do not affect or have only a small effect on the distribution of the reaction products. Removal of elementary steps that are the sole producers of a given product

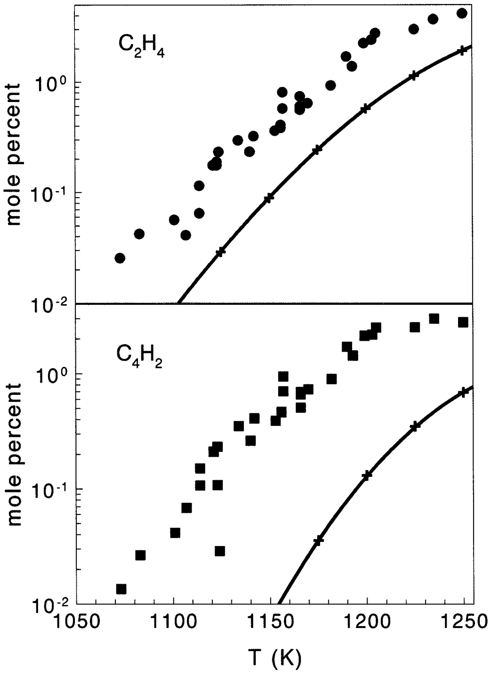


Figure 14. Calculated (lines) and experimental yields of ethylene and diacetylene. The calculations are done at 25 K interval, marked on the lines as crosses. The agreement here is unsatisfactory.

or are part of a consecutive chain that is the only route for a product formation reduces the concentration of that product almost to zero. It should be mentioned, however, that the sensitivity analysis is done by removing a single reaction at a time. When a group of reactions are removed from the scheme, there can be a strong effect on particular products although the elimination of one step alone, as is shown in Table 4, might not have an affect at all. These reactions are left in the kinetic scheme also for completeness and applicability beyond the temperature range of the present investigation where they might be more important.

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