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

## Assa Lifshitz,\* Aya Suslensky, and Carmen Tamburu

Department of Physical Chemistry, The Hebrew University, Jerusalem 91904, Israel Received: January 16, 2003; In Final Form: April 2, 2003

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<sup>3</sup>. A plethora of decomposition products, both with and without nitrogen, were found in the postshock mixtures. They were, among the nitrogen containing products: pyridine, two isomers of methylpyrrole, 2-picoline, 5-picoline, HCN, CH<sub>3</sub>CN, C<sub>2</sub>H<sub>3</sub>CN, C<sub>2</sub>H<sub>5</sub>CN, and CH≡C−CN. Very small quantities of *cis*- and trans-CH<sub>3</sub>CH=CHCN and CH<sub>2</sub>=CHCH<sub>2</sub>CN were also found in the post-shock mixtures. Among the products without nitrogen were CH<sub>4</sub>,  $C_2H_4$ ,  $C_2H_6$ ,  $C_2H_2$ , CH<sub>3</sub>C=CH, CH<sub>2</sub>=C=CH<sub>2</sub>,  $C_4H_4$  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<sup>3</sup> 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<sub>3</sub>CN, 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<sup>-1</sup>. 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<sup>1-5</sup> and its methyl derivatives<sup>6-8</sup> 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.<sup>7</sup> 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 2,4dimethylpyrrole 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  $\sim \pm 1$  °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  $3 \times 10^{-5}$ 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-

<sup>\*</sup> To whom correspondence should be addressed.

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<sub>2</sub> + HF is a first-order unimolecular reaction with a rate constant<sup>13</sup>  $k_{\rm first} = 10^{14.85}$  exp-(-74.05 × 10<sup>3</sup>/*RT*) s<sup>-1</sup>.

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

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

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

$$\chi = [CH_2 = CF_2]_t / ([CH_2 = CF_2]_t + [CH_3 CF_3]_t)$$
(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  $5 \times 10^{-5}$  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:

$$C_{5}(\text{pr})_{i} = A(\text{pr}_{i})/S(\text{pr}_{i})\{C_{5}(2,4-\text{dimethylpyrrole})_{0}\}/A(2,4-\text{dimethylpyrrole})_{0} \text{ (III)}$$

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

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

In these relations that are based on carbon atom conservation,  $C_5(2,4\text{-dimethylpyrrole})_0$  is the concentration of 2,4-dimethylpyrrole behind the reflected shock wave prior to decomposition and  $A(2,4\text{-dimethylpyrrole})_0$  is the calculated GC peak area of 2,4-dimethylpyrrole prior to decomposition (eq V) where  $A(\text{pr}_i)_t$ 



**Figure 1.** Gas chromatograms of a shock sample of 0.3% 2,4dimethylpyrrole 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.

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.  $\rho_5/\rho_1$  is the compression behind the reflected shock wave, and  $T_1$  is room temperature, 110 °C in this study.

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<sub>2</sub>), irrespective of the number of its carbon atoms. Products of very small quantities such as C<sub>4</sub> compounds other than C<sub>4</sub>H<sub>4</sub> and C<sub>4</sub>H<sub>2</sub> and C<sub>5</sub> 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

						Product	ts without Nit	rogen				
no.	<i>T</i> <sub>5</sub> (K)	$C_5 \times 1$	0 <sup>5</sup> t	t(ms)	DMP	CH <sub>4</sub>	$C_2H_4$	$C_2H_6$	$C_2H_2$	$C_3H_4$	$C_4H_4$	$C_4H_2$
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	11/0	2.55		1.50	68.29 50.79	7.43	0.643	5.10	0.293	0.330	0.157	0.735
23	1182	2.46		1.00	59.78	/.80	0.933	0.12	0.453	0.547	0.214	0.904
24	1190	2.40		2.18	42.42	10.65	1./1	9.51	1.07	0.775	0.374	1.72
25	1193	2.47		2.0	25 45	10.45	1.59	9.10	0.770	0.70	0.310	1.44
20	1199	2.52		2.0	28 21	12.00	2.20	11.77	1.47	1.00	0.400	2.14
27	1205	2.43		1.09	30.21	11.40	2.42	13.46	1.70	1.02	0.491	2.19
20	1205	2.40		1.90	24 21	17.45	2.78	12.40	2.28	1.20	0.558	2.52
30	1225	2.30		1.75	17.09	13.00	3.01	13.00	2.26	1.20	0.010	3.01
31	1250	2.55		1.68	12.98	12.0	4 18	11.50	3 77	1.40	0.754	2.80
51		2.00					1.10	11.00	5.11	1.00	0.115	2.00
				1100		1210						
				1100		Produ	cts with Nitro	gen				
no.	T <sub>5</sub> (K)	DMP	HCN	СНО	CCN	Produ CH <sub>3</sub> CN	cts with Nitro C <sub>2</sub> H <sub>3</sub> CN	gen C <sub>2</sub> H <sub>5</sub> CN	pyridine	MP	2-picoline	5-picoline
no.	T <sub>5</sub> (K)	DMP 98.12	HCN 0.0302	СНО	CCN	Produ CH <sub>3</sub> CN 0.0247	cts with Nitro $C_2H_3CN$ 0.0031	gen C <sub>2</sub> H <sub>5</sub> CN	pyridine	MP 0.0918	2-picoline	5-picoline
no.	T <sub>5</sub> (K) 1073 1083	DMP 98.12 97.10	HCN 0.0302 0.0232	СНО	CCN	Produ CH <sub>3</sub> CN 0.0247 0.0422	cts with Nitro $C_2H_3CN$ 0.0031 0.0052	gen C <sub>2</sub> H <sub>5</sub> CN	pyridine 0.146 0.242	MP 0.0918 0.0803	2-picoline 0.436 0.622	5-picoline 0.242 0.312
no.	T <sub>5</sub> (K) 1073 1083 1101	DMP 98.12 97.10 95.58	HCN 0.0302 0.0232 0.0457	СНО	CCN	Produ CH <sub>3</sub> CN 0.0247 0.0422 0.0795	cts with Nitro $C_2H_3CN$ 0.0031 0.0052 0.0087	ogen C <sub>2</sub> H <sub>5</sub> CN	pyridine 0.146 0.242 0.472	MP 0.0918 0.0803 0.154	2-picoline 0.436 0.622 1.05	5-picoline 0.242 0.312 0.444
no.	T <sub>5</sub> (K) 1073 1083 1101 1107	DMP 98.12 97.10 95.58 94.97	HCN 0.0302 0.0232 0.0457 0.0251	СНО	CCN	Produ CH <sub>3</sub> CN 0.0247 0.0422 0.0795 0.0788	cts with Nitro C <sub>2</sub> H <sub>3</sub> CN 0.0031 0.0052 0.0087 0.0057	gen C <sub>2</sub> H <sub>5</sub> CN 0.0024 0.0039	pyridine 0.146 0.242 0.472 0.521	MP 0.0918 0.0803 0.154 0.411	2-picoline 0.436 0.622 1.05 1.09	5-picoline 0.242 0.312 0.444 0.395
no. 1 2 3 4 5	T <sub>5</sub> (K) 1073 1083 1101 1107 1114	DMP 98.12 97.10 95.58 94.97 93.17	HCN 0.0302 0.0232 0.0457 0.0251 0.0425	СНО	CCN	Produ CH <sub>3</sub> CN 0.0247 0.0422 0.0795 0.0788 0.117	cts with Nitro C <sub>2</sub> H <sub>3</sub> CN 0.0031 0.0052 0.0087 0.0057 0.0057 0.0026	gen C <sub>2</sub> H <sub>5</sub> CN 0.0024 0.0039	pyridine 0.146 0.242 0.521 0.521 0.823	MP 0.0918 0.0803 0.154 0.411 0.383	2-picoline 0.436 0.622 1.05 1.09 1.55	5-picoline 0.242 0.312 0.444 0.395 0.440
no. 1 2 3 4 5 6	T <sub>5</sub> (K) 1073 1083 1101 1107 1114 1114	DMP 98.12 97.10 95.58 94.97 93.17 91.36	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407	СНО	CCN	Produ CH <sub>3</sub> CN 0.0247 0.0422 0.0795 0.0788 0.117 0.127	cts with Nitro C <sub>2</sub> H <sub>3</sub> CN 0.0031 0.0052 0.0087 0.0057 0.0026 0.0101	gen C <sub>2</sub> H <sub>5</sub> CN 0.0024 0.0039 0.0075	pyridine 0.146 0.242 0.472 0.521 0.823 1.02	MP 0.0918 0.0803 0.154 0.411 0.383 0.273	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538
no. 1 2 3 4 5 6 7	T <sub>5</sub> (K) 1073 1083 1101 1107 1114 1114 1114	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122	СНО	CCN	Produ CH <sub>3</sub> CN 0.0247 0.0795 0.0795 0.117 0.127 0.190	cts with Nitro C <sub>2</sub> H <sub>3</sub> CN 0.0031 0.0052 0.0087 0.0057 0.0026 0.0101 0.0283	gen C <sub>2</sub> H <sub>5</sub> CN 0.0024 0.0039 0.0075 0.0121	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911
no. 1 2 3 4 5 6 7 8	T <sub>5</sub> (K) 1073 1083 1101 1107 1114 1114 1121 1123	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.140	СНО	CCN	Produ CH <sub>3</sub> CN 0.0247 0.0422 0.0795 0.0788 0.117 0.127 0.190 0.194	cts with Nitro C <sub>2</sub> H <sub>3</sub> CN 0.0031 0.0052 0.0087 0.0057 0.0026 0.0101 0.0283 0.0252	gen C <sub>2</sub> H <sub>5</sub> CN 0.0024 0.0039 0.0075 0.0121 0.0161	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34
no. 1 2 3 4 5 6 7 8 9	T <sub>5</sub> (K) 1073 1083 1101 1107 1114 1114 1121 1123 1123	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.140 0.221	СНО	CCN	Produ CH <sub>3</sub> CN 0.0247 0.0422 0.0795 0.0788 0.117 0.127 0.190 0.194 0.268	cts with Nitro C <sub>2</sub> H <sub>3</sub> CN 0.0031 0.0052 0.0087 0.0057 0.0026 0.0101 0.0283 0.0252 0.0842	gen C <sub>2</sub> H <sub>5</sub> CN 0.0024 0.0039 0.0075 0.0121 0.0161 0.0089	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13
no. 1 2 3 4 5 6 7 8 9 10	T <sub>5</sub> (K) 1073 1083 1101 1107 1114 1114 1121 1123 1123 1124	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71	HCN 0.0302 0.0232 0.0457 0.0457 0.0407 0.1422 0.140 0.221 0.154	CHO	CCN	Produ CH <sub>3</sub> CN 0.0247 0.0422 0.0795 0.0788 0.117 0.127 0.190 0.194 0.268 0.195	$\begin{array}{c} \text{cts with Nitro}\\ \hline C_2H_3CN\\ \hline 0.0031\\ 0.0052\\ 0.0087\\ 0.0057\\ 0.0026\\ 0.0101\\ 0.0283\\ 0.0252\\ 0.0842\\ 0.0274\\ \end{array}$	gen C <sub>2</sub> H <sub>5</sub> CN 0.0024 0.0039 0.0075 0.0121 0.0161 0.0089 0.0173	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454
no. 1 2 3 4 5 6 7 8 9 10 11	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1114 \\ 1121 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89	HCN 0.0302 0.0232 0.0457 0.0425 0.0407 0.122 0.140 0.221 0.154 0.283	CHO	CCN	Produ CH <sub>3</sub> CN 0.0247 0.0422 0.0795 0.0788 0.117 0.127 0.190 0.194 0.268 0.195 0.298	$\begin{array}{c} \text{cts with Nitro}\\ \hline C_2H_3CN\\ \hline 0.0031\\ 0.0052\\ 0.0087\\ 0.0057\\ 0.0026\\ 0.0101\\ 0.0283\\ 0.0252\\ 0.0842\\ 0.0274\\ 0.0274\\ 0.0414 \end{array}$	gen C <sub>2</sub> H <sub>5</sub> CN 0.0024 0.0039 0.0075 0.0121 0.0161 0.0089 0.0173 0.0295	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23
no. 1 2 3 4 5 6 7 8 9 10 11 12	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1114 \\ 1121 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.140 0.221 0.154 0.283 0.264	CH( 0.00	CCN 0079	Produ CH <sub>3</sub> CN 0.0247 0.0422 0.0795 0.0788 0.117 0.127 0.190 0.194 0.268 0.195 0.298 0.254	$\begin{array}{c} \text{cts with Nitro}\\ \hline C_2H_3CN\\ \hline 0.0031\\ 0.0052\\ 0.0087\\ 0.0057\\ 0.0026\\ 0.0101\\ 0.0283\\ 0.0252\\ 0.0842\\ 0.0274\\ 0.0414\\ 0.0293\\ \end{array}$	gen C <sub>2</sub> H <sub>5</sub> CN 0.0024 0.0039 0.0075 0.0121 0.0161 0.0089 0.0173 0.0295 0.0182	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31
no. 1 2 3 4 5 6 7 8 9 10 11 12 13	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1114 \\ 1121 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.140 0.221 0.154 0.283 0.264 0.342	CH( 0.00 0.00	CCN 0079 0089	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c} \text{cts with Nitro}\\ \hline C_2H_3CN\\ \hline 0.0031\\ 0.0052\\ 0.0087\\ 0.0057\\ 0.0026\\ 0.0101\\ 0.0283\\ 0.0252\\ 0.0842\\ 0.0274\\ 0.0414\\ 0.0293\\ 0.0379\\ \end{array}$	gen C <sub>2</sub> H <sub>3</sub> CN 0.0024 0.0039 0.0075 0.0121 0.0161 0.0089 0.0173 0.0295 0.0182 0.0290	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1114 \\ 1121 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.140 0.221 0.154 0.283 0.264 0.342 0.353	CH( 0.00 0.00	CCN 0079 0089	Produ CH <sub>3</sub> CN 0.0247 0.0422 0.0795 0.0788 0.117 0.127 0.190 0.194 0.268 0.195 0.298 0.254 0.325 0.40	$\begin{array}{c} \text{cts with Nitro}\\ \hline C_2H_3\text{CN}\\ \hline 0.0031\\ 0.0052\\ 0.0087\\ 0.0057\\ 0.0026\\ 0.0101\\ 0.0283\\ 0.0252\\ 0.0842\\ 0.0274\\ 0.0414\\ 0.0293\\ 0.0379\\ 0.0639\\ \end{array}$	gen C <sub>2</sub> H <sub>3</sub> CN 0.0024 0.0039 0.0075 0.0121 0.0161 0.0089 0.0173 0.0295 0.0182 0.0290 0.0403	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15	$\begin{array}{c} T_5(K) \\ 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1114 \\ 1121 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \\ 1156 \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21 78.0	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.140 0.221 0.124 0.283 0.264 0.342 0.342 0.342	CH( 0.00 0.00	CCN 0079 0089	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{array}{c} \text{cts with Nitro}\\ \hline C_2H_3CN\\ \hline 0.0031\\ 0.0052\\ 0.0087\\ 0.0057\\ 0.0026\\ 0.0101\\ 0.0283\\ 0.0252\\ 0.0842\\ 0.0274\\ 0.0414\\ 0.0293\\ 0.0379\\ 0.0639\\ 0.0609\\ \end{array}$	$\begin{array}{c} \text{gen} \\ \hline C_2 H_5 \text{CN} \\ \hline 0.0024 \\ 0.0039 \\ \hline 0.0075 \\ 0.0121 \\ 0.0161 \\ 0.0089 \\ 0.0173 \\ 0.0295 \\ 0.0182 \\ 0.0290 \\ 0.0403 \\ 0.0457 \\ \end{array}$	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98 3.34	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870 1.26	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66 4.01	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88 2.13
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16	$\begin{array}{c} T_5(K) \\ 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1121 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \\ 1156 \\ 1156 \\ 1156 \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21 78.0 78.91	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.140 0.221 0.154 0.283 0.264 0.342 0.342 0.353 0.336 0.454	CH( 0.00 0.00	CCN 0079 0089	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{array}{c} \text{cts with Nitro}\\ \hline C_2H_3CN\\ \hline 0.0031\\ 0.0052\\ 0.0087\\ 0.0057\\ 0.0026\\ 0.0101\\ 0.0283\\ 0.0252\\ 0.0842\\ 0.0274\\ 0.0414\\ 0.0293\\ 0.0379\\ 0.0639\\ 0.0639\\ 0.0609\\ 0.0536\\ \end{array}$	$\begin{array}{c} \text{gen} \\ \hline C_2 H_5 \text{CN} \\ \hline 0.0024 \\ 0.0039 \\ \hline 0.0075 \\ 0.0121 \\ 0.0161 \\ 0.0089 \\ 0.0173 \\ 0.0295 \\ 0.0182 \\ 0.0290 \\ 0.0403 \\ 0.0457 \\ 0.0385 \\ \hline \end{array}$	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98 3.34 3.11	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870 1.26 0.654	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66 4.01 3.74	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88 2.13 1.59
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1121 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \\ 1156 \\ 1156 \\ 1156 \\ 1157 \\ \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21 78.0 78.91 68.14	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.140 0.221 0.154 0.283 0.264 0.342 0.353 0.336 0.454 0.432	CH0 0.00 0.00 0.00	CCN 0079 0089 040 .72	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{array}{c} \text{cts with Nitro}\\ \hline C_2H_3CN\\ \hline 0.0031\\ 0.0052\\ 0.0087\\ 0.0057\\ 0.0026\\ 0.0101\\ 0.0283\\ 0.0252\\ 0.0842\\ 0.0274\\ 0.0414\\ 0.0293\\ 0.0379\\ 0.0639\\ 0.0639\\ 0.0609\\ 0.0536\\ 0.151\\ \hline \end{array}$	gen C <sub>2</sub> H <sub>5</sub> CN 0.0024 0.0039 0.0075 0.0121 0.0161 0.0089 0.0173 0.0295 0.0182 0.0290 0.0403 0.0457 0.0385 0.106	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98 3.34 3.11 4.39	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870 1.26 0.654 0.964	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66 4.01 3.74 4.90	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88 2.13 1.59 1.51
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 8	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1114 \\ 1121 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \\ 1156 \\ 1156 \\ 1157 \\ 1157 \\ 1157 \\ 1157 \\ \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21 78.0 78.91 68.14 72.98	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.140 0.221 0.154 0.283 0.264 0.353 0.356 0.454 0.432 0.386	CH0 0.00 0.00 0.01 0.00	CCN 0079 0089 040 172 144	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{array}{c} \text{cts with Nitro}\\ \hline C_2H_3\text{CN}\\ \hline 0.0031\\ 0.0052\\ 0.0087\\ 0.0057\\ 0.0026\\ 0.0101\\ 0.0283\\ 0.0252\\ 0.0842\\ 0.0274\\ 0.0414\\ 0.0293\\ 0.0379\\ 0.0639\\ 0.0639\\ 0.0639\\ 0.0536\\ 0.151\\ 0.107\\ 0.0614\end{array}$	gen C <sub>2</sub> H <sub>5</sub> CN 0.0024 0.0039 0.0075 0.0121 0.0161 0.0089 0.0173 0.0295 0.0182 0.0290 0.0403 0.0457 0.0385 0.106 0.0859 0.0859	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98 3.34 3.11 4.39 4.53	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870 1.26 0.654 0.964 1.11	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66 4.01 3.74 4.90 4.85	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88 2.13 1.59 1.51 1.73
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 2	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1114 \\ 1121 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \\ 1156 \\ 1156 \\ 1157 \\ 1157 \\ 1157 \\ 1166 \\ 1166 \\ 1157 \\ 1166 $	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21 78.0 78.91 68.14 72.98 71.05	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.154 0.221 0.154 0.223 0.364 0.342 0.342 0.353 0.336 0.454 0.432 0.386 0.454	CH0 0.00 0.00 0.01 0.00 0.01 0.00 0.00	CCN 0079 0089 040 172 044 0370	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{array}{c} \text{cts with Nitro}\\ \hline C_2H_3\text{CN}\\ \hline 0.0031\\ 0.0052\\ 0.0087\\ 0.0057\\ 0.0026\\ 0.0101\\ 0.0283\\ 0.0252\\ 0.0842\\ 0.0274\\ 0.0274\\ 0.0414\\ 0.0293\\ 0.0379\\ 0.0639\\ 0.0639\\ 0.0639\\ 0.0536\\ 0.151\\ 0.107\\ 0.0944\\ 0.0944\\ \end{array}$	$\begin{array}{c} \text{gen} \\ \hline C_2 H_5 \text{CN} \\ \hline 0.0024 \\ 0.0039 \\ \hline 0.0075 \\ 0.0121 \\ 0.0161 \\ 0.0089 \\ 0.0173 \\ 0.0295 \\ 0.0182 \\ 0.0290 \\ 0.0403 \\ 0.0457 \\ 0.0385 \\ 0.106 \\ 0.0859 \\ 0.0763 \\ 0.0763 \\ \hline 0.0763 \\ \hline 0.0765 \\ \hline 0.0755 \\ \hline 0.0765 \\ \hline 0.0765 \\ \hline 0.0755 \\ \hline 0.0755$	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98 3.34 3.11 4.39 4.53 4.76	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870 1.26 0.654 0.964 1.11 1.52	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66 4.01 3.74 4.90 4.85 5.17	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88 2.13 1.59 1.51 1.73 2.66
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1114 \\ 1121 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \\ 1156 \\ 1156 \\ 1156 \\ 1157 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21 78.0 78.91 68.14 72.98 71.05 69.71	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.154 0.221 0.154 0.283 0.264 0.342 0.353 0.356 0.454 0.432 0.386 0.468 0.707	CH( 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.	CCN 0079 0089 140 172 144 1370 134	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{array}{c} \text{cts with Nitro}\\ \hline C_2H_3\text{CN}\\ \hline 0.0031\\ 0.0052\\ 0.0087\\ 0.0057\\ 0.0026\\ 0.0101\\ 0.0283\\ 0.0252\\ 0.0842\\ 0.0274\\ 0.0414\\ 0.0293\\ 0.0379\\ 0.0639\\ 0.0639\\ 0.0639\\ 0.0536\\ 0.151\\ 0.107\\ 0.0944\\ 0.0933\\ \end{array}$	$\begin{array}{c} \text{gen} \\ \hline C_2 H_3 \text{CN} \\ \hline 0.0024 \\ 0.0039 \\ \hline 0.0075 \\ 0.0121 \\ 0.0161 \\ 0.0089 \\ 0.0173 \\ 0.0295 \\ 0.0182 \\ 0.0290 \\ 0.0403 \\ 0.0457 \\ 0.0385 \\ 0.106 \\ 0.0859 \\ 0.0763 \\ 0.0695 \\ 0.0695 \\ \hline 0.0695 \\ $	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98 3.34 3.11 4.39 4.53 4.76 5.19	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870 1.26 0.654 0.964 1.11 1.52 1.63	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66 4.01 3.74 4.90 4.85 5.17 5.29	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88 2.13 1.59 1.51 1.73 2.66 2.66 2.66
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 2	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1114 \\ 1121 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \\ 1156 \\ 1156 \\ 1156 \\ 1157 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1157 \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21 78.0 78.01 68.14 72.98 71.05 69.71 67.30 67.30	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.154 0.221 0.154 0.283 0.264 0.342 0.353 0.366 0.458 0.386	CH( 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.	CCN 0079 0089 040 172 044 0370 034 140 0320	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{array}{c} \text{cts with Nitro}\\ \hline C_2H_3\text{CN}\\ \hline 0.0031\\ 0.0052\\ 0.0087\\ 0.0057\\ 0.0026\\ 0.0101\\ 0.0283\\ 0.0252\\ 0.0842\\ 0.0274\\ 0.0414\\ 0.0293\\ 0.0379\\ 0.0639\\ 0.0639\\ 0.0639\\ 0.0536\\ 0.151\\ 0.107\\ 0.0944\\ 0.0933\\ 0.313\\ 0.313\\ 0.313\\ 0.313\end{array}$	$\begin{array}{c} \text{gen} \\ \hline C_2 H_3 \text{CN} \\ \hline 0.0024 \\ 0.0039 \\ \hline 0.0075 \\ 0.0121 \\ 0.0161 \\ 0.0089 \\ 0.0173 \\ 0.0295 \\ 0.0182 \\ 0.0290 \\ 0.0403 \\ 0.0457 \\ 0.0385 \\ 0.106 \\ 0.0859 \\ 0.0763 \\ 0.0695 \\ 0.0860 \\ 0.$	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98 3.34 3.11 4.39 4.53 4.76 5.19 5.31 5.57	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870 1.26 0.654 0.964 1.11 1.52 1.63 1.68 1.45	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66 4.01 3.74 4.90 4.85 5.17 5.29 6.27	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88 2.13 1.59 1.51 1.73 2.66 2.66 3.34
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 22	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1114 \\ 1121 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \\ 1156 \\ 1156 \\ 1156 \\ 1157 \\ 1157 \\ 1156 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1160 \\ 1102 \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21 78.0 78.01 68.14 72.98 71.05 69.71 67.30 68.29 67.2	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.154 0.221 0.154 0.283 0.264 0.342 0.353 0.356 0.458 0.468 0.707 1.22 0.831 1.51	CH( 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.	CCN CCN 0079 0089 040 172 144 1370 034 140 039 022	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	cts with Nitro $C_2H_3CN$ 0.0031 0.0052 0.0087 0.0057 0.0026 0.0101 0.0283 0.0252 0.0842 0.0274 0.0274 0.0274 0.0274 0.0273 0.0379 0.0639 0.0609 0.0536 0.151 0.107 0.0944 0.0933 0.313 0.109 0.551	$\begin{array}{c} \text{gen} \\ \hline C_2 H_3 \text{CN} \\ \hline 0.0024 \\ 0.0039 \\ \hline 0.0075 \\ 0.0121 \\ 0.0161 \\ 0.0089 \\ 0.0173 \\ 0.0295 \\ 0.0182 \\ 0.0290 \\ 0.0403 \\ 0.0457 \\ 0.0385 \\ 0.106 \\ 0.0859 \\ 0.0763 \\ 0.0695 \\ 0.0860 \\ 0.0798 \\ 0.156 \\ \hline \end{array}$	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98 3.34 3.11 4.53 4.53 4.76 5.19 5.31 5.67 5.02	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870 1.26 0.654 0.964 1.11 1.52 1.63 1.68 1.45 2.12	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66 4.01 3.74 4.90 4.85 5.17 5.29 6.27 5.53	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88 2.13 1.59 1.51 1.73 2.66 2.66 3.34 2.68
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 4	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1114 \\ 1121 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \\ 1156 \\ 1156 \\ 1156 \\ 1157 \\ 1157 \\ 1157 \\ 1156 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1170 \\ 1182 \\ 1100 \\ 1182 \\ 1100 \\ 1182 \\ 1100 \\ 1182 \\ 1100 \\ 1182 \\ 1100 \\ 1182 \\ 1100 \\ 1182 \\ 1100 \\ 1182 \\ 1100 \\ 1182 \\ 1100 \\ 1182 \\ 1100 \\ 1182 \\ 1100 \\ 1182 \\ 1100 \\ 1182 \\ 1100 \\ 1182 \\ 1100 \\ 1182 \\ 1100 $	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21 78.0 78.91 68.14 72.98 71.05 69.71 67.30 68.29 59.78 42.42	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.140 0.283 0.264 0.342 0.353 0.336 0.454 0.432 0.386 0.468 0.707 1.22 0.831 1.04	CH( 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.	CCN CCN 0079 0089 040 172 044 0370 034 040 039 082	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	cts with Nitro $C_2H_3CN$ 0.0031 0.0052 0.0087 0.0057 0.0026 0.0101 0.0283 0.0252 0.0842 0.0274 0.0274 0.0414 0.0293 0.0379 0.0639 0.0609 0.0536 0.151 0.107 0.0944 0.0933 0.313 0.109 0.254 0.254	$\begin{array}{c} \text{gen} \\ \hline C_2 H_5 \text{CN} \\ \hline 0.0024 \\ 0.0039 \\ \hline 0.0075 \\ 0.0121 \\ 0.0161 \\ 0.0089 \\ 0.0173 \\ 0.0295 \\ 0.0182 \\ 0.0290 \\ 0.0403 \\ 0.0457 \\ 0.0385 \\ 0.106 \\ 0.0859 \\ 0.0763 \\ 0.0695 \\ 0.0860 \\ 0.0798 \\ 0.159 \\ 0.159 \\ 0.202 \\ \end{array}$	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98 3.34 3.11 4.39 4.53 4.76 5.19 5.31 5.67 8.02 1.25	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870 1.26 0.654 0.964 1.11 1.52 1.63 1.68 1.45 2.13 2.52	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66 4.01 3.74 4.90 4.85 5.17 5.29 6.27 5.53 6.98 8.55 1.75 5.29 6.27 5.53 6.98	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88 2.13 1.59 1.51 1.73 2.66 2.66 3.34 2.68 3.67
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 23 24 25 20 21 22 23 24 22 23 24 22 23 24 25 20 20 21 22 23 24 25 20 20 20 20 20 20 20 20 20 20	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1117 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \\ 1156 \\ 1156 \\ 1156 \\ 1156 \\ 1157 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1170 \\ 1182 \\ 1190 \\ 1102 \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21 78.0 78.01 68.14 72.98 71.05 69.71 67.30 68.29 59.78 42.42 59.78	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.140 0.221 0.154 0.283 0.264 0.342 0.336 0.454 0.336 0.454 0.336 0.454 0.336 0.454 0.336 0.457 0.336 0.452 0.336 0.452 0.336 0.452 0.336 0.452 0.345 0.345 0.345 0.345 0.345 0.345 0.345 0.345 0.345 0.345 0.345 0.455 0.345 0.355	CH0 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	CCN CCN 0079 0089 040 172 144 0370 034 140 039 082 199 000	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{array}{c} \text{cts with Nitro}\\ \hline C_2H_3CN\\ \hline 0.0031\\ 0.0052\\ 0.0087\\ 0.0057\\ 0.0026\\ 0.0101\\ 0.0283\\ 0.0252\\ 0.0842\\ 0.0274\\ 0.0414\\ 0.0293\\ 0.0609\\ 0.0536\\ 0.151\\ 0.107\\ 0.0944\\ 0.0933\\ 0.313\\ 0.109\\ 0.254\\ 0.393\\ 0.254\\ 0.393\\ 0.351\\ 0.254\\ 0.393\\ 0.351\\ 0.$	$\begin{array}{c} \text{gen} \\ \hline C_2 H_5 \text{CN} \\ \hline 0.0024 \\ 0.0039 \\ \hline 0.0075 \\ 0.0121 \\ 0.0161 \\ 0.0089 \\ 0.0173 \\ 0.0295 \\ 0.0182 \\ 0.0290 \\ 0.0403 \\ 0.0457 \\ 0.0385 \\ 0.106 \\ 0.0859 \\ 0.0763 \\ 0.0695 \\ 0.0763 \\ 0.0695 \\ 0.0860 \\ 0.0798 \\ 0.159 \\ 0.309 \\ 0.20 \\ \end{array}$	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98 3.34 3.11 4.39 4.53 4.76 5.19 5.31 5.67 8.02 12.34 0.22	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870 1.26 0.654 0.964 1.11 1.52 1.63 1.68 1.45 2.13 2.52 2.83	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66 4.01 3.74 4.90 4.85 5.17 5.29 6.27 5.53 6.98 8.59 6.72	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88 2.13 1.59 1.51 1.73 2.66 2.66 3.34 2.68 3.67 4.87 2.64
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1117 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \\ 1156 \\ 1156 \\ 1156 \\ 1157 \\ 1156 \\ 1156 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1170 \\ 1182 \\ 1190 \\ 1193 \\ 1100 \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21 78.0 78.0 78.0 78.91 68.14 72.98 71.05 69.71 67.30 68.29 59.78 42.42 50.11 25.45	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.140 0.221 0.154 0.283 0.264 0.353 0.356 0.356 0.336 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.422 0.386 0.454 0.422 0.386 0.454 0.422 0.386 0.454 0.422 0.386 0.454 0.422 0.386 0.454 0.422 0.386 0.454 0.422 0.386 0.454 0.422 0.386 0.454 0.422 0.386 0.454 0.422 0.575 0.222 0.575 0.326 0.454 0.422 0.575 0.326 0.454 0.422 0.575	CH0 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	CCN CCN 0079 0089 040 .72 044 0370 034 040 039 082 299 80 82 299 80	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{array}{c} \text{cts with Nitro}\\ \hline C_2H_3CN\\ \hline 0.0031\\ 0.0052\\ 0.0087\\ 0.0057\\ 0.0026\\ 0.0101\\ 0.0283\\ 0.0252\\ 0.0842\\ 0.0274\\ 0.0414\\ 0.0293\\ 0.0379\\ 0.0639\\ 0.0639\\ 0.0639\\ 0.0639\\ 0.0536\\ 0.151\\ 0.107\\ 0.0944\\ 0.0933\\ 0.313\\ 0.109\\ 0.254\\ 0.393\\ 0.254$	$\begin{array}{c} \text{gen} \\ \hline C_2 H_5 \text{CN} \\ \hline 0.0024 \\ 0.0039 \\ \hline 0.0075 \\ 0.0121 \\ 0.0161 \\ 0.0089 \\ 0.0173 \\ 0.0295 \\ 0.0182 \\ 0.0290 \\ 0.0403 \\ 0.0457 \\ 0.0385 \\ 0.106 \\ 0.0859 \\ 0.0763 \\ 0.0695 \\ 0.0860 \\ 0.0798 \\ 0.159 \\ 0.309 \\ 0.20 \\ 0.$	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98 3.34 3.11 4.39 4.53 4.76 5.19 5.31 5.67 8.02 12.34 9.33 4.55 12.34 9.33	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870 1.26 0.654 0.964 1.11 1.52 1.63 1.68 1.45 2.13 2.52 2.81 2.60	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66 4.01 3.74 4.90 4.85 5.17 5.29 6.27 5.53 6.98 8.59 6.78 8.78	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88 2.13 1.59 1.51 1.73 2.66 2.66 3.34 2.68 3.67 4.87 3.84 4.57
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 27	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1117 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \\ 1156 \\ 1156 \\ 1157 \\ 1156 \\ 1156 \\ 1157 \\ 1157 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1170 \\ 1182 \\ 1190 \\ 1193 \\ 1199 \\ 1202 \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21 78.0 78.0 78.01 68.14 72.98 71.05 69.71 67.30 68.29 59.78 42.42 50.11 35.45 28.21	HCN 0.0302 0.0457 0.0251 0.0425 0.0407 0.122 0.140 0.221 0.154 0.283 0.364 0.353 0.336 0.454 0.432 0.386 0.454 0.432 0.386 0.468 0.707 1.22 0.831 1.04 1.49 1.55 2.30	CH0 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	CCN CCN 0079 0089 040 172 044 0370 034 040 039 082 299 80 0337 126	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{array}{c} \text{cts with Nitro}\\ \hline C_2H_3\text{CN}\\ \hline 0.0031\\ 0.0052\\ 0.0087\\ 0.0057\\ 0.0026\\ 0.0101\\ 0.0283\\ 0.0252\\ 0.0842\\ 0.0274\\ 0.0414\\ 0.0293\\ 0.0639\\ 0.0639\\ 0.0639\\ 0.0639\\ 0.0639\\ 0.0639\\ 0.0536\\ 0.151\\ 0.107\\ 0.0944\\ 0.0933\\ 0.313\\ 0.109\\ 0.0254\\ 0.393\\ 0.254\\ 0.393\\ 0.254\\ 0.579\\ 0.602\\ \end{array}$	$\begin{array}{c} \text{gen} \\ \hline C_2 H_5 \text{CN} \\ \hline 0.0024 \\ 0.0039 \\ \hline 0.0075 \\ 0.0121 \\ 0.0161 \\ 0.0089 \\ 0.0173 \\ 0.0295 \\ 0.0182 \\ 0.0290 \\ 0.0403 \\ 0.0457 \\ 0.0385 \\ 0.106 \\ 0.0859 \\ 0.0763 \\ 0.0695 \\ 0.0860 \\ 0.0798 \\ 0.159 \\ 0.309 \\ 0.20 \\ 0.382 \\ 0.406 \\ \end{array}$	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98 3.34 3.11 4.39 4.53 4.76 5.19 5.31 5.67 8.02 12.34 9.33 12.25 12.20	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870 1.26 0.654 0.964 1.11 1.52 1.63 1.68 1.45 2.13 2.52 2.81 2.60 2.46	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66 4.01 3.74 4.90 4.85 5.17 5.29 6.27 5.53 6.98 8.59 6.78 8.36 7.68	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88 2.13 1.59 1.51 1.73 2.66 2.66 3.34 2.68 3.67 4.87 3.84 4.56 4.49
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1114 \\ 1121 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \\ 1156 \\ 1156 \\ 1157 \\ 1157 \\ 1156 \\ 1156 \\ 1156 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1170 \\ 1182 \\ 1190 \\ 1193 \\ 1199 \\ 1203 \\ 1205 \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21 78.0 78.91 68.14 72.98 71.05 69.71 67.30 68.29 59.78 42.42 50.11 35.45 38.21 20.01	HCN 0.0302 0.0457 0.0251 0.0425 0.0407 0.122 0.140 0.221 0.154 0.283 0.264 0.353 0.356 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.448 0.707 1.22 0.831 1.04 1.49 1.55 2.30 1.67 2.12	CHO 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.	0079 0089 040 172 044 0370 034 040 039 082 299 180 037 136 022	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	cts with Nitro $C_2H_3CN$ 0.0031 0.0052 0.0087 0.0057 0.0026 0.0101 0.0283 0.0252 0.0842 0.0274 0.0274 0.0274 0.0274 0.0273 0.0639 0.0639 0.0609 0.0536 0.151 0.107 0.0944 0.0933 0.313 0.109 0.254 0.393 0.254 0.579 0.602 0.612 0.	$\begin{array}{c} \text{gen} \\ \hline C_2 H_5 \text{CN} \\ \hline 0.0024 \\ 0.0039 \\ \hline 0.0075 \\ 0.0121 \\ 0.0161 \\ 0.0089 \\ 0.0173 \\ 0.0295 \\ 0.0182 \\ 0.0290 \\ 0.0403 \\ 0.0403 \\ 0.0457 \\ 0.0385 \\ 0.106 \\ 0.0859 \\ 0.0763 \\ 0.0695 \\ 0.0860 \\ 0.0798 \\ 0.159 \\ 0.309 \\ 0.20 \\ 0.382 \\ 0.406 \\ 0.409 \\ \end{array}$	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98 3.34 3.11 4.39 4.53 4.76 5.19 5.31 5.67 8.02 12.34 9.33 12.45 13.29 11.82	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870 1.26 0.654 0.964 1.11 1.52 1.63 1.63 1.45 2.13 2.52 2.81 2.60 2.46 2.98	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66 4.01 3.74 4.90 4.85 5.17 5.29 6.27 5.53 6.98 8.59 6.78 8.36 7.68 7.50	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88 2.13 1.59 1.51 1.73 2.66 2.66 3.34 2.68 3.67 4.87 3.84 4.56 4.48
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1117 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \\ 1156 \\ 1156 \\ 1156 \\ 1156 \\ 1156 \\ 1157 \\ 1157 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1170 \\ 1182 \\ 1190 \\ 1193 \\ 1199 \\ 1203 \\ 1205 \\ 1225 \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21 78.0 78.91 68.14 72.98 71.05 69.71 67.30 68.29 59.78 42.42 50.11 35.45 38.21 30.91 24.21	HCN 0.0302 0.0457 0.0251 0.0425 0.0407 0.122 0.154 0.221 0.154 0.283 0.366 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.448 0.707 1.22 0.831 1.04 1.55 2.30 1.67 3.13 2.01	CHO CHO 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.	CCN CCN 0079 0089 040 172 044 0370 034 040 039 034 040 039 035 136 037 136 037 136 037 136 037 136	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	cts with Nitro $C_2H_3CN$ 0.0031 0.0052 0.0087 0.0057 0.0026 0.0101 0.0283 0.0252 0.0842 0.0274 0.0274 0.0274 0.0274 0.0273 0.0379 0.0639 0.0609 0.0536 0.151 0.107 0.0944 0.0933 0.313 0.109 0.254 0.393 0.254 0.393 0.254 0.393 0.254 0.393 0.254 0.579 0.602 0.643 0.767	$\begin{array}{c} \text{gen} \\ \hline C_2 H_5 \text{CN} \\ \hline 0.0024 \\ 0.0039 \\ \hline 0.0075 \\ 0.0121 \\ 0.0161 \\ 0.0089 \\ 0.0173 \\ 0.0295 \\ 0.0182 \\ 0.0290 \\ 0.0403 \\ 0.0457 \\ 0.0385 \\ 0.106 \\ 0.0763 \\ 0.0695 \\ 0.0763 \\ 0.0695 \\ 0.0763 \\ 0.0798 \\ 0.159 \\ 0.309 \\ 0.20 \\ 0.382 \\ 0.406 \\ 0.408 \\ 0.520 \\ \end{array}$	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98 3.34 3.11 4.39 4.53 4.76 5.19 5.31 5.67 8.02 12.34 9.33 12.45 13.29 11.83 17.45	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870 1.26 0.654 0.964 1.11 1.52 1.63 1.68 1.45 2.13 2.52 2.81 2.60 2.46 2.98 2.96	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66 4.01 3.74 4.90 4.85 5.17 5.29 6.27 5.53 6.98 8.59 6.78 8.36 7.68 7.59 9.36	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88 2.13 1.59 1.51 1.73 2.66 2.66 3.34 2.68 3.67 4.87 3.84 4.56 4.48 4.18 5.70
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30	$\begin{array}{c} T_5(K) \\ \hline 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1117 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \\ 1156 \\ 1156 \\ 1156 \\ 1156 \\ 1157 \\ 1157 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1193 \\ 1199 \\ 1203 \\ 1205 \\ 1225 \\ 1235 \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21 78.0 78.91 68.14 72.98 71.05 69.71 67.30 68.29 59.78 42.42 50.11 35.45 38.21 30.91 24.21 17.09	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.154 0.221 0.154 0.283 0.366 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.454 0.432 0.386 0.455 0.336 0.454 0.432 0.336 0.455 0.336 0.457 0.336 0.457 0.336 0.457 0.336 0.457 0.336 0.457 0.336 0.457 0.336 0.457 0.336 0.457 0.432 0.336 0.457 0.432 0.336 0.457 0.457 0.336 0.457 0.457 0.457 0.336 0.454 0.452 0.336 0.454 0.452 0.336 0.455 0.455 0.336 0.455 0.336 0.455 0.336 0.455 0.336 0.455 0.336 0.455 0.336 0.455 0.336 0.455 0.336 0.455 0.336 0.455 0.336 0.455 0.336 0.455 0.336 0.455 0.336 0.455 0.336 0.455 0.336 0.455 0.367 0.336 0.455 0.336 0.455 0.336 0.455 0.336 0.455 0.336 0.455 0.367 0.336 0.367 0.336 0.367 0.336 0.367 0.330 0.367 0.336 0.367 0.330 0.367 0.331 0.301 0.353 0.353 0.356 0.353 0.355	CHO CHO 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.	0079 0079 0089 040 72 044 0370 034 040 039 082 299 180 037 136 663 796 18	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	cts with Nitro $C_2H_3CN$ 0.0031 0.0052 0.0087 0.0057 0.0026 0.0101 0.0283 0.0252 0.0842 0.0274 0.0274 0.0274 0.0274 0.0274 0.0273 0.0639 0.0639 0.0609 0.0536 0.151 0.107 0.0944 0.0933 0.313 0.109 0.254 0.393 0.254 0.393 0.254 0.393 0.254 0.393 0.254 0.393 0.254 0.393 0.254 0.393 0.254 0.393 0.254 0.393 0.254 0.393 0.254 0.393 0.254 0.393 0.254 0.393 0.254 0.393 0.254 0.393 0.257 0.602 0.643 0.767 0.927	$\begin{array}{c} \text{gen} \\ \hline C_2 H_5 \text{CN} \\ \hline 0.0024 \\ 0.0039 \\ \hline 0.0075 \\ 0.0121 \\ 0.0161 \\ 0.0089 \\ 0.0173 \\ 0.0295 \\ 0.0182 \\ 0.0290 \\ 0.0403 \\ 0.0457 \\ 0.0385 \\ 0.106 \\ 0.0859 \\ 0.0763 \\ 0.0695 \\ 0.0763 \\ 0.0695 \\ 0.0763 \\ 0.0695 \\ 0.0798 \\ 0.159 \\ 0.309 \\ 0.20 \\ 0.382 \\ 0.406 \\ 0.408 \\ 0.529 \\ 0.631 \\ \end{array}$	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98 3.34 3.11 4.39 4.53 4.76 5.19 5.31 5.67 8.02 12.34 9.33 12.45 13.29 11.83 17.45 19.07	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870 1.26 0.654 0.964 1.11 1.52 1.63 1.68 1.45 2.13 2.52 2.81 2.60 2.46 2.98 2.96 2.86	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66 4.01 3.74 4.90 4.85 5.17 5.29 6.27 5.53 6.98 8.59 6.78 8.36 7.68 7.59 9.36 9.10	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88 2.13 1.59 1.51 1.73 2.66 2.66 3.34 2.68 3.67 4.87 3.84 4.56 4.48 4.18 5.70 5.08
no. 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 4	$\begin{array}{c} T_5(K) \\ 1073 \\ 1083 \\ 1101 \\ 1107 \\ 1114 \\ 1114 \\ 1121 \\ 1123 \\ 1123 \\ 1124 \\ 1134 \\ 1140 \\ 1142 \\ 1153 \\ 1156 \\ 1156 \\ 1156 \\ 1156 \\ 1157 \\ 1157 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1166 \\ 1160 \\ 1182 \\ 1190 \\ 1193 \\ 1199 \\ 1203 \\ 1205 \\ 1225 \\ 1235 \\ 1250 \end{array}$	DMP 98.12 97.10 95.58 94.97 93.17 91.36 88.75 87.41 88.88 87.71 82.89 85.61 80.07 80.21 78.0 78.91 68.14 72.98 71.05 69.71 67.30 68.29 59.78 42.42 50.11 35.45 38.21 30.91 24.21 17.09 12.98	HCN 0.0302 0.0232 0.0457 0.0251 0.0425 0.0407 0.122 0.154 0.221 0.154 0.283 0.364 0.342 0.353 0.364 0.454 0.432 0.386 0.454 0.432 0.386 0.468 0.707 1.22 0.831 1.04 1.55 2.30 1.67 3.13 3.01 3.53 5.22	CH0 CH0 0.00 0.00 0.00 0.00 0.00 0.00 0.	CCN CCN 0079 0089 040 72 044 0370 034 044 0370 034 044 0370 034 039 999 880 537 136 663 796 63 796 08 0	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	cts with Nitro $C_2H_3CN$ 0.0031 0.0052 0.0087 0.0057 0.0026 0.0101 0.0283 0.0252 0.0842 0.0274 0.0274 0.0274 0.0414 0.0293 0.0379 0.0639 0.0639 0.0639 0.0536 0.151 0.107 0.0944 0.0933 0.313 0.109 0.254 0.393 0.254 0.393 0.254 0.579 0.602 0.643 0.767 0.927 1.49	$\begin{array}{c} \text{gen} \\ \hline C_2 H_3 \text{CN} \\ \hline 0.0024 \\ 0.0039 \\ \hline 0.0075 \\ 0.0121 \\ 0.0161 \\ 0.0089 \\ 0.0173 \\ 0.0295 \\ 0.0182 \\ 0.0290 \\ 0.0403 \\ 0.0457 \\ 0.0385 \\ 0.106 \\ 0.0859 \\ 0.0763 \\ 0.0695 \\ 0.0860 \\ 0.0798 \\ 0.159 \\ 0.309 \\ 0.20 \\ 0.382 \\ 0.406 \\ 0.408 \\ 0.529 \\ 0.631 \\ 0.917 \\ \end{array}$	pyridine 0.146 0.242 0.472 0.521 0.823 1.02 1.16 1.56 1.40 1.25 2.20 1.95 3.01 2.98 3.34 3.11 4.39 4.53 4.76 5.19 5.31 5.67 8.02 12.34 9.33 12.45 13.29 11.83 17.45 19.07 22.89	MP 0.0918 0.0803 0.154 0.411 0.383 0.273 0.665 0.751 0.210 0.553 1.03 0.695 1.09 0.870 1.26 0.654 0.964 1.11 1.52 1.63 1.68 1.45 2.13 2.52 2.81 2.60 2.46 2.98 2.96 2.86 3.09	2-picoline 0.436 0.622 1.05 1.09 1.55 1.82 1.95 2.31 2.71 1.94 2.96 2.83 3.68 3.66 4.01 3.74 4.90 4.85 5.17 5.29 6.27 5.53 6.98 8.59 6.78 8.36 7.68 7.59 9.36 9.19 9.01	5-picoline 0.242 0.312 0.444 0.395 0.440 0.538 0.911 1.34 1.13 0.454 1.23 1.31 1.67 1.88 2.13 1.59 1.51 1.73 2.66 2.66 3.34 2.68 3.67 4.87 3.84 4.56 4.48 4.18 5.70 5.08 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

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



**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.

products, calculated from the relation

$$k_{\text{product}} = \frac{[\text{product}]_{i}}{[2,4\text{-dimethyl pyrrole}]_{0} - [2,4\text{-dimethyl pyrrole}]_{t}^{k_{\text{total}}}}$$
(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<sup>3</sup> carbons) and dissociation of methyl groups from the pyrrole ring:

$$\overset{CH_{3}}{\swarrow} \underset{H}{\overset{CH_{3}}{\longrightarrow}} \overset{CH_{3}}{\underset{H}{\overset{CH_{3}}{\longrightarrow}}} \overset{CH_{3}}{\underset{H}{\overset{CH_{2}}{\longrightarrow}}} * H^{*}$$
(1)

$$\overset{CH_{3}}{\swarrow} \underset{H}{\overset{CH_{3}}{\longrightarrow}} \overset{CH_{2}}{\overset{\bullet}{\longleftarrow}} \underset{H}{\overset{CH_{3}}{\longrightarrow}} \overset{+}{\overset{H}} \overset{+}{\overset{H}} \overset{(2)}{\overset{(2)}{\longrightarrow}}$$

$$\overset{CH_{3}}{\longleftarrow} \underset{H}{\overset{CH_{3}}{\longrightarrow}} \overset{CH_{3}}{\underset{H}{\longrightarrow}} \overset{CH_{3}}{\underset{H}{\longrightarrow}} \overset{CH_{3}}{\underset{H}{\longrightarrow}}$$
(3)



 TABLE 2: First Order Arrhenius Parameters for the

 Production Rates of the Various Reaction Products

no.	products	$\log A$ (s <sup>-1</sup> )	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 <sub>3</sub> CN	16.02	82.0
12	C <sub>2</sub> H <sub>3</sub> CN	21.20	113.0
13	C <sub>2</sub> H <sub>5</sub> CN	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<sup>2</sup> 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:



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<sup>8</sup> 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.<sup>7</sup> 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.<sup>7</sup> In the transition state, in addition to N-Cbond 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 2,4dimethylpyrrole. 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  $\sim$ 35 kcal/mol, compared to 61 and 74 kcal/mol for the other two.<sup>7</sup> We have also found (yet unpublished) that the isomerization barrier for the isomerization from the 2 position to the N position is equal to  $\sim$ 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<sup>14-17</sup> 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<sup>3</sup>, s<sup>-1</sup>, kcal, and mol<sup>-1</sup>. 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.<sup>18</sup> The parameters for

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

no	reactions	$A(s^{-1})$	<i>E</i> (kcal/mol)	k <sub>f</sub> (1150 К)	k <sub>r</sub> (1150 K)	Δ <i>S</i> <sub>r</sub> (1150 K)	Δ <i>H</i> <sub>r</sub> (1150 K)	ref
1	$DMPvrrole \rightarrow DMPvrrole(R1)^{\bullet} + H^{\bullet}$	$3.0 \times 10^{15}$	78	4.52	$4.64 \times 10^{14}$	30.8	83.0	est
2	DMPyrrole $\rightarrow$ DMPyrrole(R2)• + H•	$3.0 \times 10^{15}$	78	4.52	$4.64\times10^{14}$	30.8	83.0	est
3	$DMPyrrole \rightarrow MPyrrole(R1)^{\bullet} + CH_{3}^{\bullet}$	$4.0 \times 10^{16}$	80	25.1	$3.52 \times 10^{12}$	46.7	86.1	est
4	$DMPyrrole \rightarrow MPyrrole(R2)^{\bullet} + CH_{3}^{\bullet}$	$4.0 \times 10^{16}$	80	25.1	$3.52 \times 10^{12}$	46.7	86.1	est
5 6	DMPyrrole + $H^{\bullet} \rightarrow DMPyrrole(R1)^{\bullet} + H_2$ DMPyrrole + $H^{\bullet} \rightarrow DMPyrrole(R2)^{\bullet} + H_2$	$1.20 \times 10^{14}$ 1.20 × 10 <sup>14</sup>	9	$2.34 \times 10^{12}$ 2.34 × 10^{12}	$1.38 \times 10^{7}$ $1.38 \times 10^{7}$	3.34 3.34	-23.7 -23.7	est
7	DMPyrrole + $CH_3^{\bullet} \rightarrow DMPyrrole(R1)^{\bullet} + CH_4$	$1.0 \times 10^{13}$	15	$1.41 \times 10^{10}$	$1.50 \times 10^{-1.54} \times 10^{-6}$	-3.40	-24.8	est
8	DMPyrrole + $CH_3^{\bullet} \rightarrow DMPyrrole(R2)^{\bullet} + CH_4$	$1.0 \times 10^{13}$	15	$1.41 \times 10^{10}$	$1.54  imes 10^6$	-3.40	-24.8	est
9	$DMPyrrole + H^{\bullet} \rightarrow 2-MPyrrole + CH_{3}^{\bullet}$	$1.0 \times 10^{14}$	8	$3.02 \times 10^{12}$	$6.66 \times 10^{8}$	7.23	-10.9	est
10	DMPyrrole + $H^{\bullet} \rightarrow 4$ -MPyrrole + $CH_{3}^{\bullet}$	$1.0 \times 10^{14}$	8	$3.02 \times 10^{12}$	$6.66 \times 10^{8}$	7.23	-10.9	est
11	DMPyrrole(R1) $\rightarrow$ CH <sub>3</sub> CN + C <sub>4</sub> H <sub>5</sub> $\rightarrow$ DMPyrrole(R2) $\rightarrow$ CH <sub>3</sub> CN + C <sub>4</sub> H <sub>5</sub> $\rightarrow$	$2.50 \times 10^{13}$ $2.50 \times 10^{13}$	68 68	2.99	$4.48 \times 10^{7}$ $4.48 \times 10^{7}$	40.6 40.6	58.3 58.3	est
12	DMP yrrole(R1)• $\rightarrow$ C <sub>3</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>4</sub> CN•	$8.0 \times 10^{13}$	60	317.0	$4.48 \times 10^{7}$	44.8	52.4	est
14	$DMPyrrole(R2)^{\bullet} \rightarrow C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$	$8.0 \times 10^{13}$	60	317.0	$4.48 \times 10^7$	44.8	52.4	est
15	$MPyrrole(R1)^{\bullet} \rightarrow HCN + C_4H_5^{\bullet}$	$2.50 \times 10^{13}$	60	99.1	$1.22 \times 10^9$	32.1	48.1	est
16	$MPyrrole(R2)^{\bullet} \rightarrow HCN + C_4H_5^{\bullet}$	$2.50 \times 10^{13}$	60	99.1	$1.22 \times 10^9$	32.1	48.1	est
17	$MPyrrole(R1)^{\bullet} \rightarrow C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R2)^{\bullet} \rightarrow C_{4}H_{4} + CH_{2}CN^{\bullet}$	$2.50 \times 10^{13}$	62.5	33.2	$1.43 \times 10^{7}$	34.3	43.0	est
10	$MPyrrole(R2) \rightarrow C_3H_4 + CH_2CN$ $MPyrrole(R1)^{\bullet} \rightarrow CH_2CN + C_2H_2^{\bullet}$	$2.30 \times 10^{13}$ 2.50 × 10^{13}	60 60	99 1	$1.43 \times 10^{7}$ $4.87 \times 10^{7}$	33.2	43.0 41.9	est
20	$MPyrrole(R2)^{\bullet} \rightarrow CH_3CN + C_3H_3^{\bullet}$	$2.50 \times 10^{13}$ $2.50 \times 10^{13}$	60	99.1	$4.87 \times 10^{7}$	33.2	41.9	est
21	DMPyrrole(R1)• + H• $\rightarrow$ MPyrrole(R3)• + CH <sub>3</sub> •	$1.0 \times 10^{14}$	7	$4.68 \times 10^{12}$	$8.68 \times 10^{8}$	7.54	-11.0	est
22	$DMPyrrole(R2)^{\bullet} + H^{\bullet} \rightarrow MPyrrole(R4)^{\bullet} + CH_{3}^{\bullet}$	$1.0 \times 10^{14}$	7	$4.68 \times 10^{12}$	$8.68 \times 10^8$	7.54	-11.0	est
23	$MPyrrole(R3) \bullet \rightarrow C_2H_3 + C_2H_3CN$	$2.50 \times 10^{13}$	78	0.0376	$6.21 \times 10^{6}$	44.3	68.1	est
24	$MPyrrole(R4)^{\bullet} \rightarrow C_2H_3 + C_2H_3CN$	$2.50 \times 10^{13}$	78	0.0376	$6.21 \times 10^{6}$	44.3	68.1	est
25	$MPyrrole(R3)^{\bullet} \rightarrow C_{2}H_{2} + C_{2}H_{4}CN^{\bullet}$ $MPyrrole(R4)^{\bullet} \rightarrow C_{2}H_{2} + C_{2}H_{4}CN^{\bullet}$	$2.50 \times 10^{13}$ 2.50 × 10^{13}	65 65	11.1 11.1	$1.20 \times 10^7$ $1.20 \times 10^7$	43.0	55.1	est
20	$MPyrrole(R3)^{\bullet} \rightarrow HCN + C_4H_{\epsilon}^{\bullet}$	$2.50 \times 10^{13}$	72	0.520	$4.71 \times 10^{7}$	40.5	62.2	est
28	$MPyrrole(R4)^{\bullet} \rightarrow HCN + C_4H_5^{\bullet}$	$2.50 \times 10^{13}$	72	0.520	$4.71 \times 10^{7}$	40.5	62.2	est
29	DMPyrrole(R1)• $\rightarrow$ 5-Picoline + H•	$1.62 \times 10^{13}$	50.6	$3.89 \times 10^{3}$	$7.34  imes 10^{10}$	21.0	36.3	est
30	$DMPyrrole(R2)^{\bullet} \rightarrow 2$ -Picoline + H•	$6.0 \times 10^{13}$	47	$7.03 \times 10^4$	$1.32 \times 10^{12}$	21.0	36.3	est
31	$MPyrrole(R1)^{\bullet} \rightarrow Pyridine + H^{\bullet}$	$1.0 \times 10^{13}$	60	39.6	$9.67 \times 10^{8}$	11.1	25.5	est
32	$MPyrrole(R2)^{\bullet} \rightarrow Pyridine + H^{\bullet}$	$1.0 \times 10^{13}$	60	39.6	$9.67 \times 10^{8}$	11.1	25.5	est
33 34	$MPyrrole(R3)^{\bullet} \rightarrow Pyrldine + H^{\bullet}$ $MPyrrole(R4)^{\bullet} \rightarrow Pyrldine + H^{\bullet}$	$5.0 \times 10^{13}$ $5.0 \times 10^{13}$	48 48	$3.78 \times 10^{4}$ $3.78 \times 10^{4}$	$6.78 \times 10^{12}$ $6.78 \times 10^{12}$	19.4 19.4	39.6 39.6	7, mod. 7 mod
35	2-Picoline + $H^{\bullet} \rightarrow Pvridine + CH_{2}^{\bullet}$	$2.0 \times 10^{14}$	40 7	$9.35 \times 10^{12}$	$1.65 \times 10^{10}$	5.96	-7.64	est
36	5-Picoline + $H^{\bullet} \rightarrow$ Pyridine + $CH_{3}^{\bullet}$	$2.0 \times 10^{14}$	7	$9.35 \times 10^{12}$	$1.65 \times 10^{10}$	5.96	-7.64	est
37	$MPyrrole(R1)^{\bullet} + H^{\bullet} \rightarrow 4-MPyrrole$	$1.0 \times 10^{14}$	0	$1.0 \times 10^{14}$	0.157	-39.4	-97.1	est
38	$MPyrrole(R2)^{\bullet} + H^{\bullet} \rightarrow 2-MPyrrole$	$1.0 \times 10^{14}$	0	$1.0 \times 10^{14}$	0.157	-39.4	-97.1	est
39	$MPyrrole(R3)^{\bullet} + H^{\bullet} \rightarrow 2-MPyrrole$	$1.0 \times 10^{14}$	0	$1.0 \times 10^{14}$	1.16	-31.1	-82.9	est
40	$MPyrrole(R4)^{\bullet} + H^{\bullet} \rightarrow 4-MPyrrole$ $2 MPyrrole + H^{\bullet} \rightarrow MPyrrole(P3)^{\bullet} + H_{\bullet}$	$1.0 \times 10^{14}$ $3.0 \times 10^{14}$	0 10	$1.0 \times 10^{14}$ 3.77 $\times 10^{12}$	1.16 $1.87 \times 10^{7}$	-31.1	-82.9 -23.7	est
42	4-MPvrrole + $H^{\bullet} \rightarrow MPvrrole(R4)^{\bullet} + H_2$	$3.0 \times 10^{14}$	10	$3.77 \times 10^{12}$	$1.87 \times 10^{7}$ $1.87 \times 10^{7}$	3.65	-23.7	est
43	2-MPyrrole + $CH_3^{\bullet} \rightarrow MPyrrole(R3)^{\bullet} + CH_4$	$5.0 \times 10^{13}$	8	$1.51 \times 10^{12}$	$1.39 \times 10^{8}$	-3.09	-24.8	8, mod.
44	4-MPyrrole + $CH_3^{\bullet} \rightarrow MPyrrole(R4)^{\bullet} + CH_4$	$5.0 \times 10^{13}$	8	$1.51 \times 10^{12}$	$1.39  imes 10^8$	-3.09	-24.8	8, mod.
45	$C_4H_5^{\bullet} \rightarrow C_4H_4 + H^{\bullet}$	$5.0 \times 10^{13}$	51	$1.02 \times 10^{4}$	$1.40 \times 10^{12}$	29.7	50.8	18, mod.
46	$C_4H_5^{\bullet} + H^{\bullet} \rightarrow C_4H_6$	$1.0 \times 10^{14}$	0	$1.0 \times 10^{14}$	$1.60 \times 10^{-2}$	-30.4	-91.9	est
47	$C_4H_3^{\bullet} + H^{\bullet} \rightarrow C_4H_4$	$3.0 \times 10^{14}$	0	$3.0 \times 10^{14}$ 2.75 × 10 <sup>7</sup>	$2. \times 10^{-4}$	-33.0	-107.4	18, mod.
40 49	$C_4H_3 \rightarrow C_4H_2 + H_2$ $C_4H_4 + H^{\bullet} \rightarrow C_4H_3^{\bullet} + H_2$	$5.0 \times 10^{14}$	9	$2.73 \times 10^{10}$ 9.74 × 10 <sup>12</sup>	$3.33 \times 10^{10}$ 8 14 × 10 <sup>11</sup>	24.2 5.57	0.727	10 29 mod
50	$C_2H_6 + H^\bullet \rightarrow C_2H_5^\bullet + H_2$	$1.43 \times 10^{14}$	9.56	$2.18 \times 10^{12}$	$5.21 \times 10^{9}$	8.18	-4.39	18
51	$C_4H_4 + H^\bullet \rightarrow C_2H_2 + C_2H_3^\bullet$	$5.0  imes 10^{14}$	7	$2.34 \times 10^{13}$	$3.78  imes 10^{11}$	6.79	-1.63	est
52	$C_3H_4 + H^\bullet \rightarrow CH_3^\bullet + C_2H_2$	$5.0 \times 10^{14}$	7	$2.34 \times 10^{13}$	$3.32 \times 10^{10}$	5.82	-8.30	18, mod.
53	$C_2H_6 + CH_3^{\bullet} \rightarrow C_2H_5^{\bullet} + CH_4$	1.64 <i>T</i> <sup>4</sup>	8.29	$7.64 \times 10^{10}$	$3.39 \times 10^9$	1.44	-5.47	24
54	$CH_4 + Ar \rightarrow CH_3^{\bullet} + H^{\bullet} + Ar(R)$ $CH_4 + H^{\bullet} \rightarrow CH_3^{\bullet} + H_4(R)$	$1.50 \times 10^{17}$ 1.44 × 10 <sup>14</sup>	88.6	2.24	$2.10 \times 10^{10}$	34.2 6.74	107.7	21
55 56	$CH_4 + H \rightarrow CH_3 + H_2(K)$ $CH_2 + CH_2 \rightarrow C_2H_2$	$1.44 \times 10^{15}$ $1.01 \times 10^{15} T^{-0.64}$	0	$1.11 \times 10^{13}$	$3.03 \times 10^{-3}$ 4.62 × 10^{-1}	-40.4	-90.7	10 26
57	$CH_3^{\bullet} + CH_3^{\bullet} \rightarrow C_2H_5^{\bullet} + H^{\bullet}$	$3.01 \times 10^{13}$	13.5	$8.14 \times 10^{10}$	$1.41 \times 10^{14}$	-4.80	11.5	26
58	$CH_3^{\bullet} + CH_3^{\bullet} \rightarrow C_2H_4 + H_2$	$4.72 \times 10^{15}$	30.8	$6.59 \times 10^{9}$	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	$1.79 \times 10^{6}$	$1.21 \times 10^{13}$	24.7	38.2	24
60	$C_2H_3^{\bullet} \rightarrow C_2H_2 + H^{\bullet}$	$2.0 \times 10^{14}$	39.7	$5.71 \times 10^{6}$	$4.26 \times 10^{13}$	23.7	37.3	26
61	$CH_3CN \rightarrow CH_2CN^{\bullet} + H^{\bullet}(R)$	$1.00 \times 10^{15}$	93	$2.12 \times 10^{-3}$	$5.20 \times 10^{12}$	34.1	94.0	28
62 62	$CH_{3}CN + H' \rightarrow CH_{3} + HCN$ $CH_{2}CN + CH_{2} + CH_{4} + CH_{4}CN'$	$1.0 \times 10^{14}$ $3.0 \times 10^{12}$	12	$4.08 \times 10^{12}$ $1.57 \times 10^{10}$	$5.20 \times 10^{7}$	/.35 _0.080	-127	27, mod.
64	$CH_3CN + H^{\bullet} \rightarrow H_2 + CH_3CN^{\bullet}$	$2.0 \times 10^{14}$	7	$9.35 \times 10^{12}$	$1.31 \times 10^9$	6 65	-12.6	28
65	$CH_2CN^{\bullet} + CH_3^{\bullet} \rightarrow C_2H_5CN$	$3.0 \times 10^{12}$	0	$3.0 \times 10^{12}$	1.70	-39.5	-83.7	27, mod.
66	$C_2H_5CN + H^\bullet \rightarrow C_2H_4CN^\bullet + H_2$	$5.0 \times 10^{14}$	7	$2.34 \times 10^{13}$	$5.67 \times 10^8$	6.65	-16.6	28, mod.
67	$C_2H_4CN \rightarrow C_2H_3CN + H^{\bullet}$	$3.0 \times 10^{13}$	50	$9.45 \times 10^{3}$	$1.07 \times 10^{13}$	25.0	50.2	28, mod.
68	$C_2H_3CN + H^{\bullet} \rightarrow H_2 + CH = CHCN^{\bullet}$	$5.0 \times 10^{14}$	9	$9.74 \times 10^{12}$	$2.24 \times 10^{12}$	3.68	0.870	28, mod.
69	$CH=CHCN^* \rightarrow CH=CCN + H^*$	$1.0 \times 10^{15}$	40	$2.50 \times 10^{\circ}$	$2.27 \times 10^{14}$	23.8	48.3	28

### TABLE 3 (Continued)

			G	lossary			
DMPyrrole:	CH <sub>3</sub> N CH <sub>3</sub>	2-Picoline:	CH3	DMPyrrole(R1)*:	CH <sub>3</sub> N H CH <sub>2</sub> •	MPyrrole(R2)*:	N H H
2-Mpyrrole:	CH <sub>3</sub>	5-Picoline:	CH <sub>3</sub>	DMPyrrole(R2)*:	CH <sub>2</sub> · N H	MPyrrole(R3)*:	CH <sub>2</sub> •
4-Mpyrrole:	CH <sub>3</sub> N H	C₃H₄:	$CH_3-C=CH + CH_2=C=CH_2$	MPyrrole(R1)*:	CH <sub>3</sub> N H	MPyrrole(R4)*:	CH <sub>2</sub> • N H





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.<sup>19–21</sup> Some were estimated using NIST–Standard Reference Data Base 25<sup>22</sup> (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



**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.

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 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  $\mu$ s. 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 1 after some 900  $\mu$ s.



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<sup>a</sup>

			A. Pro	oducts with l	Nitrogen						
no.	reactions	2-MPyrrole	4-MPyrrole	2-picoline	5-picoline	pyridine	HCN	CH≡CCN	CH <sub>3</sub> CN	C <sub>2</sub> H <sub>3</sub> CN	C <sub>2</sub> H <sub>5</sub> CN
1	$DMPyrrole \rightarrow DMPyrrole(R1) + H^{\bullet}$	-12/-	-12/-	_/_	-20/-	-17/-	_/_	-28/-13	_/_	-18/-	_/_
2	$DMPyrrole \rightarrow DMPyrrole(R2) + H^{\bullet}$	-25/-13	-25/-13	-32/-34	-/-	-30/-18	_/_	-36/-27	-/13	-15/-	-/10
3	DMPyrrole $\rightarrow$ MPyrrole(R1) + CH <sub>3</sub> •	-/19	-15/-42	-11/-	-11/-	-30/-20	-48/-43	-18/-	-48/-43	-11/-	-57/-47
4	DMPyrrole $\rightarrow$ MPyrrole(R2) + CH <sub>3</sub> * DMPyrrole + H• $\rightarrow$ DMPyrrole(R1) + H2	-15/-42 18/13	-/19 18/13	-11/- -/-	-11/-	-30/-20	-48/-43	-18/- -/-15	-48/-43	-11/-	-5//-4/
6	DMP yrrole + H $\rightarrow$ DMP yrrole(R1) + H2 DMP yrrole(R2) + H2	-/	-/	-37/-45	-/-	21/12 —/—	_/_	/ 15	_/_	-/- 20	_/_
7	DMPyrrole + $CH_3^{\bullet} \rightarrow DMPyrrole(R1) + CH_4$	_/_	_/_	_/_	-41/-20	_/_	_/_	-35/-16	_/_	-30/-13	_/_
8	$DMPyrrole + CH_3 \bullet \rightarrow DMPyrrole(R2) + CH_4$	-20/-	-20/-	-45/-21	_/_	-15/-	_/_	-30/-	_/_	-12/-	_/_
9	DMPyrrole + $H^{\bullet} \rightarrow 2$ -MPyrrole + $CH_3^{\bullet}$	-82/-43	33/11	_/_	_/_	-23/-14	_/_	37/12	_/_	-/-	_/_
10	DMPyrrole + H $\rightarrow$ 4-MPyrrole + CH <sub>3</sub> •	33/11	-82/-43	_/_	_/_	-23/-14	_/_	37/12	_/_	-/-	_/_
13	DMPyrrole(R1) $\rightarrow$ C <sub>3</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>4</sub> CN <sup>•</sup> DMPyrrole(R2) $\rightarrow$ C <sub>3</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>4</sub> CN <sup>•</sup>	_/_ _/_	_/_ _/_	_/_	_/_ _/_	_/_ _/_	_/_ _/_	-75/-70 -26/-21	_/_	-75/-65 -24/-10	_/_ _/_
15	$MPvrrole(R1) \rightarrow HCN + C_4H_5^{\bullet}$	_/_	_/_	_/_	_/_	_/_	-49/-46	_/	-/11	_/_ 1)	_/_
16	$MPyrrole(R2) \rightarrow HCN + C_4H_5^{\bullet}$	_/_	_/_	_/_	_/_	_/_	-49/-46	_/_	-/11	_/_	_/_
17	$MPyrrole(R1) \rightarrow C_3H_4 + CH_2CN^{\bullet}$	_/_	_/_	_/_	_/_	_/_	_/_	_/_	_/_	_/_	-49/-41
18	$MPyrrole(R2) \rightarrow C_3H_4 + CH_2CN^{\bullet}$	-/-	_/_	_/_	_/_	-/-	_/_	_/_	-/-	-/-	-49/-41
19	$MPyrrole(R1) \rightarrow CH_3CN + C_3H_3^{\bullet}$ $MPyrrole(R2) \rightarrow CH_3CN + C_3H_3^{\bullet}$	_/_	_/_	_/_	_/_	_/_	_/_	_/_	-49/-48	-/-	_/_
20	$MPyrrole(R2) \rightarrow CH_3CN + C_3H_3^{-1}$ DMPyrrole(R1) $\rightarrow$ 5-Picoline + H <sup>•</sup>	_/_ _35/_27	_/_ _35/_27	-/- -13/-	-/- -99/-98	-32/-30	—/— —/13	-/- -21/47	-49/-48 -/21	-/- 45/138	—/— —/14
30	DMP yrole(R2) $\rightarrow$ 2-Picoline + H <sup>•</sup>	-50/-34	-50/-34	-99/-99	-15/-	-50/-37	-/16	-23/60	-/26	79/191	-/18
33	$MPyrrole(R3) \rightarrow Pyridine + H^{\bullet}$	_/_	-/-24	_/_	_/_	-45/-51	-/-	-/-30	-/14	_/_	-/-
34	$MPyrrole(R4) \rightarrow Pyridine + H^{\bullet}$	-/-23	_/_	_/_	_/_	-44/-51	_/_	-/-30	-/14	_/_	_/_
37	$MPyrrole(R1) + H^{\bullet} \rightarrow 4-MPyrrole$	-/-	-/-45	-/-	-/-	-/-	-/18	-/22	-/15	-/-	-/17
38	$MPyrrole(R2) + H^{\bullet} \rightarrow 2-MPyrrole$	-/-45	-/-	_/_	_/_	-/-	-/18	-/22	-/15	_/_	-/17
43	2-MPyrrole + $CH_3^{\bullet} \rightarrow MPyrrole(R3) + CH_4$ 4 MPyrrole + $CH_3^{\bullet} \rightarrow MPyrrole(R3) + CH_4$	13/72	-/-21	_/_	_/_ _/_	-42/-42	_/_ _/_	-/-19 -/-10	_/_	—/— —/—	-/12
44 45	4-Mryhole + $C_{H_3} \rightarrow Mryhole(R4) + C_{H_4}$ $C_4H_4 \rightarrow C_4H_4 + H^{\bullet}$	-/-16	-/-16	_/_	_/_	-42/-42 -/-13	_/_	-/-19 -/-23	_/_ _/10	_/_	-/12 -/-
56	$CH_3^{\bullet} + CH_3^{\bullet} \rightarrow C_2H_6$	13/-45	13/-45	61/46	49/36	167/79	-/-25	117/102	-/-31	48/38	85/-
65	$CH_2CN^{\bullet} + CH_3^{\bullet} \rightarrow C_2H_5CN$	_/_	_/_	_/_	_/_	-/-	-/-	_/_	_/_	-/-14	-99/-99
66	$C_2H_5CN + H^{\bullet} \rightarrow C_2H_4CN^{\bullet} + H_2$	_/_	_/_	_/_	_/_	_/_	_/_	_/_	_/_	-/-14	-/18
67	$C_2H_4CN \rightarrow C_2H_3CN + H^{\bullet}$	-/-	_/_	_/_	_/_	-/-	_/_	-99/-99	_/_	-99/-99	_/_
68	$C_2H_3CN + H^{\bullet} \rightarrow H_2 + CH = CHCN^{\bullet}$	_/_	_/_	_/_	_/_	_/_	_/_	-100/-100	_/_	_/_	_/_
69	$CH=CHCN \rightarrow CH=CCN + H^{2}$	_/_	_/_	_/_	_/_	_/_	_/_	-100/-100	_/_	_/_	_/_
			B. Prod	lucts without	t Nitrogen						
no	. reactions	CH	B. Prod	H <sub>4</sub> C	t Nitrogen <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>3</sub> H <sub>4</sub>	C <sub>4</sub> H <sub>6</sub>	C <sub>4</sub> l	H <sub>2</sub>	C <sub>4</sub> H <sub>4</sub>
no 1	. reactions DMPyrrole → DMPyrrole(R1) + H•	CH	B. Prod [4 C <sub>2</sub> ]	$H_4 C_4$	t Nitrogen <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>3</sub> H <sub>4</sub>	C <sub>4</sub> H <sub>6</sub>	-/-	H <sub>2</sub>	C <sub>4</sub> H <sub>4</sub>
no 1 2	. reactions $DMPyrrole \rightarrow DMPyrrole(R1) + H^{\bullet}$ $DMPyrrole \rightarrow DMPyrrole(R2) + H^{\bullet}$	-/- -10/-	B. Prod $I_4$ C <sub>2</sub> I -/- -13 $-14/$	H <sub>4</sub> C <sub>2</sub>	t Nitrogen 2H <sub>6</sub> 	C <sub>2</sub> H <sub>2</sub> 15/- 27/-11	C <sub>3</sub> H <sub>4</sub> -12/- -10/-	C <sub>4</sub> H <sub>6</sub>	-/- -21/-	H <sub>2</sub>	C <sub>4</sub> H <sub>4</sub>
no 1 2 3	. reactions DMPyrrole → DMPyrrole(R1) + H• DMPyrrole → DMPyrrole(R2) + H• DMPyrrole → MPyrrole(R1) + CH <sub>3</sub> • DMPyrrole → MPyrrole(R1) + CH <sub>3</sub> •	-/- -10/- -25/-	B. Prod $I_4$ $C_2I$ -/- -13 $-14/-19$ $-49/10$ $40/$	H <sub>4</sub> C 	2H <sub>6</sub>	C <sub>2</sub> H <sub>2</sub> 15/- 27/-11 38/-36	$C_{3}H_{4}$ -12/- -10/- -20/-23	$C_4H_6$ -/- -22/-12 -52/-43	-/- -21/- -52/-	H <sub>2</sub>	$C_4H_4$ /18 -48/-43
no 1 2 3 4 5	. reactions $DMPyrrole \rightarrow DMPyrrole(R1) + H^{\bullet}$ $DMPyrrole \rightarrow DMPyrrole(R2) + H^{\bullet}$ $DMPyrrole \rightarrow MPyrrole(R1) + CH_3^{\bullet}$ $DMPyrrole \rightarrow MPyrrole(R2) + CH_3^{\bullet}$ $DMPyrrole + H^{\bullet} \rightarrow DMPyrrole(R1) + H^{\circ}$	-/- -10/- -25/- -25/-	$\begin{array}{c c} B. Prod \\ \hline \\ I_4 & C_2 \\ \hline \\ -13 & -14/ \\ -19 & -49/ \\ -19 & -49/ \\ -19 & -49/ \\ \hline \\ -19 & -49/ \\ -19 & -49/ \\ \end{array}$	$\begin{array}{c c} \text{lucts without} \\ \hline H_4 & C_2 \\ \hline - & -/- \\ -37 & -41 \\ -37 & -41 \\ -37 & -41 \\ $	2H <sub>6</sub> 	C <sub>2</sub> H <sub>2</sub> 15/- 27/-11 38/-36 38/36	$     \begin{array}{r} \hline C_{3}H_{4} \\         -12/- \\         -10/- \\         -20/-23 \\         -20/-23 \\         -20/-19 \\         -20/-19 \\         -20/-19 \\         -20/-19 \\         -20/-19 \\         -20/-19 \\         -20/-19 \\         -20/-19 \\         -20/-19 \\         -20/-19 \\         -20/-19 \\         -20/-19 \\         -20/-19 \\         -20/-19 \\         -20/-19 \\         -20/-19 \\         -20/-19 \\         -20/-23 \\         -20/-19 \\         -20/-23 \\         -20/-23 \\         -20/-19 \\         -20/-19 \\         -20/-23 \\         -20/-23 \\         -20/-23 \\         -20/-23 \\         -20/-23 \\         -20/-23 \\         -20/-23 \\         -20/-19 \\         -20/-23 \\        $	$\begin{array}{r} C_{4}H_{6} \\ \hline -/- \\ -22/-12 \\ -52/-43 \\ -52/-43 \\ 16/11 \end{array}$	-/- -21/- -52/- -52/- 16/10	H <sub>2</sub>	
no 1 2 3 4 5 7	. reactions DMPyrrole → DMPyrrole(R1) + H• DMPyrrole → DMPyrrole(R2) + H• DMPyrrole → MPyrrole(R1) + CH <sub>3</sub> • DMPyrrole → MPyrrole(R2) + CH <sub>3</sub> • DMPyrrole + H• → DMPyrrole(R1) + H2 DMPyrrole + CH•• → DMPyrrole(R1) + C	-/- -10/- -25/- -25/- -/10 H4 - 35/-	$\begin{array}{c c} B. \ Prod \\ \hline \\ $	$\begin{array}{c c} \text{lucts without} \\ \hline H_4 & C_2 \\ \hline - & -/- \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ \hline 16/- \end{array}$	t Nitrogen 2H6 	C <sub>2</sub> H <sub>2</sub> 15/- 27/-11 38/-36 38/36	$\begin{array}{r} \hline C_{3}H_{4} \\ \hline -12/- \\ -10/- \\ -20/-23 \\ -20/-23 \\ -20/-19 \\ -23/- \end{array}$	-/- -22/-12 -52/-43 -52/-43 16/11 -/-	-/- -21/- -52/- -52/- 16/10 -/-	H <sub>2</sub>	$     C_4H_4     //-     //18     -48/-43     -48/-43     //-$
no 1 2 3 4 5 7 8	$\begin{tabular}{ c c c c } \hline reactions \\ \hline DMPyrrole $\rightarrow$ DMPyrrole(R1) + H^{\bullet}$ \\ DMPyrrole $\rightarrow$ DMPyrrole(R2) + H^{\bullet}$ \\ DMPyrrole $\rightarrow$ MPyrrole(R1) + CH_3^{\bullet}$ \\ DMPyrrole $\rightarrow$ MPyrrole(R2) + CH_3^{\bullet}$ \\ DMPyrrole + H^{\bullet} $\rightarrow$ DMPyrrole(R1) + H2$ \\ DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R1) + CH_3^{\bullet}$ \\ DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CH_3^{\bullet}$ \\ \hline DMPyrrole + CH_3^{\bullet} $\rightarrow$ \\ \hline DMPyrrole + CH_3^{\bullet} $ \\ \hline DMPyrrole$	-/- -10/ -25/ -25/ -/10 H <sub>4</sub> -35/ H <sub>4</sub> -39/	$\begin{array}{c c} B. \ \text{Prod} \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ -13 & -14/ \\ -19 & -49/ \\ -19 & -49/ \\ -19 & -49/ \\ -/- \\ -10 & 21/- \\ -12 & 13/- \\ \end{array}$	$\begin{array}{c c} \text{lucts without} \\ \hline H_4 & C_2 \\ \hline \\ - & -/- \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ 12/- \\ 12/- \end{array}$	2H <sub>6</sub> 	C <sub>2</sub> H <sub>2</sub> 15/- 27/-11 38/-36 38/36 18/- 22/-	$\begin{array}{c} \hline C_{3}H_{4} \\ \hline -12/- \\ -10/- \\ -20/-23 \\ -20/-23 \\ -20/-19 \\ -23/- \\ -/- \\ \hline \end{array}$	$\begin{array}{c} C_4H_6\\ \hline -/-\\ -22/-12\\ -52/-43\\ -52/-43\\ 16/11\\ -/-\\ -18/-\end{array}$	C <sub>4</sub> 1 -/- -21/- -52/- -52/- 16/10 -/- -18/-	H <sub>2</sub> 	C <sub>4</sub> H <sub>4</sub> /18 -48/-43 -48/-43 /- /-
no 1 2 3 4 5 7 8 9	$\begin{tabular}{ c c c c c } \hline reactions \\ \hline DMPyrrole $\rightarrow$ DMPyrrole(R1) + H^{\bullet}$ \\ DMPyrrole $\rightarrow$ DMPyrrole(R2) + H^{\bullet}$ \\ DMPyrrole $\rightarrow$ MPyrrole(R1) + CH_3^{\bullet}$ \\ DMPyrrole $\rightarrow$ MPyrrole(R2) + CH_3^{\bullet}$ \\ DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R1) + H2$ \\ DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R1) + CH_3^{\bullet}$ \\ DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + CD$ \\ DMPyrrole + H^{\bullet} $\rightarrow$ 2-MPyrrole + CH_3^{\bullet}$ \\ \end{tabular}$	-/- -10/ -25/ -25/ -/10 H <sub>4</sub> -35/ H <sub>4</sub> -39/ -10/	$\begin{array}{c c} B. Prod\\ \hline B. Prod\\ \hline I_4 & C_2 l\\ -13 & -14/\\ -19 & -49/\\ -19 & -49/\\ -19 & -49/\\ -19 & -13/\\ -13 & -13/\\ \end{array}$	Have the without $H_4$ C $H_4$ $H_4$ C $H_4$ $H$	t Nitrogen 2H6 	C <sub>2</sub> H <sub>2</sub> 15/- 27/-11 38/-36 38/36 18/- 22/- 0/-	$\begin{array}{c} \hline C_{3}H_{4} \\ \hline -12/- \\ -10/- \\ -20/-23 \\ -20/-23 \\ -20/-19 \\ -23/- \\ -/- \\ -/- \\ -/- \end{array}$	C <sub>4</sub> H <sub>6</sub> -/- -22/-12 -52/-43 16/11 -/- -18/- 27/-	C <sub>4</sub> ) -/- -52/- -52/- 16/10 -/- -18/- 26/-	H <sub>2</sub> 	C <sub>4</sub> H <sub>4</sub> /18 -48/-43 -48/-43 /- /-
no 1 2 3 4 5 7 8 9 10	$\begin{tabular}{ c c c c c } \hline reactions \\ \hline DMPyrrole $\rightarrow$ DMPyrrole(R1) + H^{\bullet}$ \\ DMPyrrole $\rightarrow$ DMPyrrole(R2) + H^{\bullet}$ \\ DMPyrrole $\rightarrow$ MPyrrole(R1) + CH_3^{\bullet}$ \\ DMPyrrole $\rightarrow$ MPyrrole(R2) + CH_3^{\bullet}$ \\ DMPyrrole + H^{\bullet} $\rightarrow$ DMPyrrole(R1) + H2$ \\ DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R1) + CD$ \\ DMPyrrole + CH_3^{\bullet} $\rightarrow$ DMPyrrole(R2) + C$ \\ DMPyrrole + H^{\bullet} $\rightarrow$ 2-MPyrrole + CH_3^{\bullet}$ \\ DMPyrrole + H $\rightarrow$ 4-MPyrrole + CH_3^{\bullet}$ \\ \hline \end{tabular}$	CH -/- -10/ -25/ -/10 H <sub>4</sub> -35/ H <sub>4</sub> -39/ -10/ -10/	$\begin{array}{c c} B. Prod\\ \hline B. Prod\\ \hline I_4 & C_2 \\ \hline -13 & -14/\\ -19 & -49/\\ -19 & -49/\\ -19 & -49/\\ -10 & 21/-\\ -10 & 21/-\\ -112 & 13/-\\ -13 & -13/\\ -13 & -13/\end{array}$	$\begin{array}{c c} \text{H}_4 & \text{C}_7 \\ \hline & -/- \\ - & -/- \\ - & -/- \\ - & -7 \\ - & -41 \\ -37 & -41 \\ -/- \\ - & -13 \\ - & -13 \\ - & -13 \end{array}$	t Nitrogen 2H <sub>6</sub> 	C <sub>2</sub> H <sub>2</sub> 15/- 27/-11 38/-36 38/36 18/- 22/- 0/-	C <sub>3</sub> H <sub>4</sub> -12/- -10/- -20/-23 -20/-23 -20/-19 -23/- -/- -/-	$\begin{array}{c} C_4H_6\\ \hline -/-\\ -22/-12\\ -52/-43\\ -52/-43\\ 16/11\\ -/-\\ -18/-\\ 27/-\\ -27/-\\ -27/-\end{array}$	C41 -/- -52/- -52/- 16/10 -/- -18/- 26/- 26/-	H <sub>2</sub> 	C <sub>4</sub> H <sub>4</sub> /- /18 -48/-43 /- /- /- /- /- /-
no 1 2 3 4 5 7 8 9 10 13 14	reactions DMPyrrole → DMPyrrole(R1) + H• DMPyrrole → DMPyrrole(R2) + H• DMPyrrole → MPyrrole(R2) + CH3• DMPyrrole → MPyrrole(R2) + CH3• DMPyrrole + H• → DMPyrrole(R1) + H2 DMPyrrole + CH3• → DMPyrrole(R1) + CD DMPyrrole + CH3• → DMPyrrole(R2) + C DMPyrrole + H• → 2-MPyrrole + CH3• DMPyrrole + H → 4-MPyrrole + CH3• DMPyrrole + H → 4-MPyrrole + CH3• DMPyrrole(R1) → C3H4 + C2H4CN•	$\begin{array}{c} CF \\ -/- \\ -10/- \\ -25/- \\ -25/- \\ -25/- \\ -100 \\ H_4 \\ -39/- \\ -10/- \\ -10/- \\ -/- \\ -/- \end{array}$	$\begin{array}{c c} B. Prod\\ \hline B. Prod\\ \hline I_4 & C_2 \\ \hline -13 & -14/\\ -19 & -49/\\ -19 & -49/\\ -19 & -49/\\ -10 & 21/-\\ -10 & 21/-\\ -13 & -13/\\ -13 & -13/\\ -13 & -13/\\ -/ \end{array}$	$\begin{array}{c c} \text{Lucts without} \\ \text{H}_4 & \text{C}_7 \\ \hline & -/- \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ 12/- \\ - & -13 \\ - & -13 \\ -/- \end{array}$	t Nitrogen 2H6 	C <sub>2</sub> H <sub>2</sub> 15/- 27/-11 38/-36 38/36 18/- 22/-	$\frac{C_{3}H_{4}}{-12/-}$ $-10/-$ $-20/-23$ $-20/-23$ $-20/-19$ $-23/-$ $-/-$ $-/-$ $-/-$ $-/-$ $-/-$ $-/-$ $-/-$ $-/-$	$\begin{array}{c} -C_4H_6\\ \hline -/-\\ -22/-12\\ -52/-43\\ -52/-43\\ 16/11\\ -/-\\ -18/-\\ 27/-\\ -27/-\\ -27/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ $	C41 -/- -52/- -52/- 16/10 -/- 26/- 26/- -/-	H <sub>2</sub> 	
no 1 2 3 4 5 7 8 9 10 13 14 15	reactions DMPyrrole → DMPyrrole(R1) + H• DMPyrrole → DMPyrrole(R2) + H• DMPyrrole → MPyrrole(R2) + CH3• DMPyrrole → MPyrrole(R1) + CH3• DMPyrrole + H• → DMPyrrole(R1) + H2 DMPyrrole + CH3• → DMPyrrole(R1) + C DMPyrrole + CH3• → DMPyrrole(R2) + C DMPyrrole + H• → 2-MPyrrole + CH3• DMPyrrole(R1) → C_3H_4 + C_2H_4CN• DMPyrrole(R2) → C_3H_4 + C_2H_4CN• DMPyrrole(R2) → C_3H_4 + C_2H_4CN• DMPyrrole(R2) → C_3H_4 + C_2H_4CN•	CH -/- -10/ -25/ -25/ -710 H <sub>4</sub> -35/ H <sub>4</sub> -39/ -10/ -10/ -10/ -/- -/-	$\begin{array}{c c} \text{B. Prod} \\ \hline \text{B. Prod} \\ \hline \text{I}_4 & \text{C}_2 \text{I} \\ \hline -13 & -14/\\ -19 & -49/\\ -19 & -49/\\ -19 & -49/\\ -10 & 21/-\\ -10 & 21/-\\ -13 & -13/\\ -13 & -13/\\ -13 & -13/\\ -/-\\ -/-\\ / \end{array}$	$\begin{array}{c c} \text{Lucts without} \\ \text{H}_4 & \text{C}_7 \\ \hline & -/- \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ -12/- \\ -13 \\13 \\ -/- \\ -/- \\ / \end{array}$	t Nitrogen 2H6 	$\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline 18/- \\ 22/- \\ 0/- \\ 22/- \\ 0/- \\ 29/- \\ 29/- \\ 25/-20 \end{array}$	$\begin{array}{c} \hline C_{3}H_{4} \\ \hline -12/- \\ -10/- \\ -20/-23 \\ -20/-23 \\ -20/-19 \\ -23/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\$	$\begin{array}{c} C_4H_6\\ \hline -/-\\ -22/-12\\ -52/-43\\ -52/-43\\ 16/11\\ -/-\\ -18/-\\ 27/-\\ -27/-\\ -27/-\\ -/-\\ -/-\\ -50/-52\\ \end{array}$	C <sub>4</sub> -/- -52/- -52/- 16/10 -/- 26/- 26/- 26/- -/- -/-	H <sub>2</sub>	
no 1 2 3 4 5 7 8 9 10 13 14 15 16	$reactions$ DMPyrrole → DMPyrrole(R1) + H• DMPyrrole → DMPyrrole(R2) + H• DMPyrrole → MPyrrole(R2) + CH3• DMPyrrole → MPyrrole(R1) + CH3• DMPyrrole + H• → DMPyrrole(R1) + H2 DMPyrrole + CH3• → DMPyrrole(R1) + CD DMPyrrole + CH3• → DMPyrrole(R2) + C DMPyrrole + H• → 2-MPyrrole + CH3• DMPyrrole + H → 4-MPyrrole + CH3• DMPyrrole(R1) → C_3H_4 + C_2H_4CN• DMPyrrole(R1) → C_3H_4 + C_2H_4CN• MPyrrole(R1) → HCN + C_4H5• MPyrrole(R2) → HCN + C_4H5•	CH -/- -10/ -25/ -25/ -/10 H <sub>4</sub> -35/ H <sub>4</sub> -35/ -10/ -10/ -10/ -/- -/- -/-	$\begin{array}{c c} \text{B. Prod} \\ \hline \text{B. Prod} \\ \hline \text{I}_4 & \text{C}_2 \text{I} \\ \hline -13 & -14/\\ -19 & -49/\\ -19 & -49/\\ -19 & -49/\\ -10 & 21/-\\ -12 & 13/-\\ -13 & -13/\\ -13 & -13/\\ -13 & -13/\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -$	$\begin{array}{c c} \text{Lucts without} \\ \text{H}_4 & \text{C}_7 \\ \hline & -/- \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ 12/- \\ -13 \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \end{array}$	t Nitrogen 2H6 	$\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline 18/- \\ 22/- \\ 0/- \\ 22/- \\ 0/- \\ 22/- \\ 22/- \\ 22/- \\ - \\ 22/- \\ 22/- \\ 39 \\ 25/-39 \\$	$\begin{array}{r} \hline C_{3}H_{4} \\ \hline -12/- \\ -10/- \\ -20/-23 \\ -20/-23 \\ -20/-19 \\ -23/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\$	$\begin{array}{c} -C_4H_6\\ \hline -/-\\ -22/-12\\ -52/-43\\ -52/-43\\ 16/11\\ -/-\\ -18/-\\ 27/-\\ -27/-\\ -/-\\ -27/-\\ -/-\\ -50/-52\\ -50/-52\end{array}$	C4 -/- -52/- -52/- 16/10 -/- 26/- 26/- 26/- -/- -50/- -50/-	H <sub>2</sub> -42 -42 -42            	$ \frac{C_4H_4}{\frac{1}{18}} $ $ \frac{48}{-43} - 43 $ $ \frac{48}{-43} - 43 $ $ \frac{48}{-43} - 43 $ $ \frac{49}{-46} - 49 - 46 $
no 1 2 3 4 5 7 8 9 10 13 14 15 16 17	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	CH -/- -10/ -25/ -25/ -25/ -10 H <sub>4</sub> -35/ H <sub>4</sub> -35/ H <sub>4</sub> -39/ -10/ -10/ -10/ -/- -/- -/-	$\begin{array}{c c} \text{B. Prod} \\ \hline \text{B. Prod} \\ \hline \text{I}_4 & \text{C}_2 \text{I} \\ \hline -13 & -14/\\ -19 & -49/\\ -19 & -49/\\ -19 & -49/\\ -10 & 21/-\\ -12 & 13/-\\ -12 & 13/-\\ -13 & -13/\\ -13 & -13/\\ -13 & -13/\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -$	$\begin{array}{c c} \text{Lucts without} \\ \text{H}_4 & \text{C}_7 \\ \hline & -/- \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ 12/- \\ -13 \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \end{array}$	t Nitrogen 2H6	C <sub>2</sub> H <sub>2</sub> 15/- 27/-11 38/-36 38/36 18/- 22/- )/- 22/-	$\begin{array}{r} \hline C_{3}H_{4} \\ \hline -12/- \\ -10/- \\ -20/-23 \\ -20/-23 \\ -20/-19 \\ -23/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/2 \\ $	$\begin{array}{c} C_4H_6\\ \hline -/-\\ -22/-12\\ -52/-43\\ -52/-43\\ 16/11\\ -/-\\ -18/-\\ 27/-\\ -27/-\\ -/-\\ -27/-\\ -/-\\ -/-\\ -50/-52\\ -50/-52\\ -/-\\ \end{array}$	$\begin{array}{c}2 \\ -21/- \\ -52/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ 26/- \\ 26/- \\ 26/- \\ -/- \\ -50/- \\ -50/- \\ -/- \\ -50/- \\ -/- \end{array}$	H <sub>2</sub> -42 -42 -42            	$ \frac{C_4H_4}{\frac{1}{18}} $ $ \frac{48}{-43} $ $ \frac{48}{-43} $ $ \frac{48}{-43} $ $ \frac{48}{-43} $ $ \frac{49}{-43} $ $ \frac{49}{-46} $ $ \frac{49}{-46} $
no 1 2 3 4 5 7 8 9 10 13 14 15 16 17 18	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{array}{c} CF \\ -/- \\ -10/- \\ -25/- \\ -25/- \\ -710 \\ H_4 \\ -35/- \\ H_4 \\ -39/- \\ -10/- \\ -10/- \\ -10/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \end{array}$	$\begin{array}{c c} \text{B. Prod} \\ \hline \text{B. Prod} \\ \hline \text{I}_4 & \text{C}_2 \\ \hline & -/- \\ -13 & -14/\\ -19 & -49/\\ -19 & -49/\\ -19 & -49/\\ -10 & 21/-\\ -12 & 13/-\\ -12 & 13/-\\ -13 & -13/\\ -13 & -13/\\ -13 & -13/\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -$	$\begin{array}{c c} \text{Lucts without} \\ \text{H}_4 & \text{C}_7 \\ \hline & -/- \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ 12/- \\ -13 \\ -/- \end{array}$	t Nitrogen 2H6	$\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline 18/- \\ 22/- \\ 0/- \\ 22/- \\ 0/- \\ 22/- \\ 22/- \\ 22/- \\ 38/36 \\ \hline 18/- \\ 22/- \\ 22/- \\ 38/36 \\ \hline 22/- \\ 38/36 \\ \hline 3$	$\begin{array}{r} \hline C_{3}H_{4} \\ \hline -12/- \\ -10/- \\ -20/-23 \\ -20/-23 \\ -20/-19 \\ -23/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/2 \\ -/2 \\ -12/-29 \\ -12/-29 \\ -12/-29 \end{array}$	$\begin{array}{c} C_4H_6 \\ \hline -/- \\ -22/-12 \\ -52/-43 \\ -52/-43 \\ 16/11 \\ -/- \\ -18/- \\ 27/- \\ -27/- \\ -/- \\ -27/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \end{array}$	C4 -/- -52/- -52/- 16/10 -/- 26/- 26/- 26/- 26/- -/- -/- -50/-  -50/- -/- -/-	H <sub>2</sub> -42 -42 -42            	$ \frac{C_4H_4}{\frac{1}{18}} $ $ \frac{48}{-43} $ $ \frac{48}{-43} $ $ \frac{48}{-43} $ $ \frac{48}{-43} $ $ \frac{49}{-43} $ $ \frac{49}{-46} $ $ \frac{49}{-46} $ $ \frac{49}{-46} $
no 1 2 3 4 5 7 8 9 10 13 14 15 16 17 18 29	$\label{eq:reactions} \hline \\ DMPyrrole \rightarrow DMPyrrole(R1) + H^{\bullet} \\ DMPyrrole \rightarrow DMPyrrole(R2) + H^{\bullet} \\ DMPyrrole \rightarrow MPyrrole(R1) + CH_3^{\bullet} \\ DMPyrrole \rightarrow MPyrrole(R1) + CH_3^{\bullet} \\ DMPyrrole + H^{\bullet} \rightarrow DMPyrrole(R1) + H2 \\ DMPyrrole + CH_3^{\bullet} \rightarrow DMPyrrole(R1) + CD \\ DMPyrrole + CH_3^{\bullet} \rightarrow DMPyrrole(R2) + CD \\ DMPyrrole + H^{\bullet} \rightarrow 2\text{-}MPyrrole + CH_3^{\bullet} \\ DMPyrrole + H \rightarrow 2\text{-}MPyrrole + CH_3^{\bullet} \\ DMPyrrole(R1) \rightarrow C_3H_4 + C_2H_4CN^{\bullet} \\ DMPyrrole(R1) \rightarrow HCN + C_4H_5^{\bullet} \\ MPyrrole(R1) \rightarrow C_3H_4 + CH_3^{\bullet} \\ MPyrrole(R1) \rightarrow C_3H_4 + CH_2CN^{\bullet} \\ MPyrrole(R1) \rightarrow C_3H_4 + CH_2CN^{\bullet} \\ MPyrrole(R1) \rightarrow C_3H_4 + CH_2CN^{\bullet} \\ MPyrrole(R1) \rightarrow 5\text{-Picoline + H^{\bullet}} \\ \hline \end{array}$	$\begin{array}{c} CF \\ \hline \\ -/- \\ -10/ \\ -25/ \\ -25/ \\ -25/ \\ -710 \\ H_4 \\ -35/ \\ H_4 \\ -39/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c} \text{Lucts without} \\ \text{H}_4 & \text{C}_7 \\ \hline & -/- \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ -12/- \\ -13 \\ -/- \\ -/ \\ -/- \\ -/- \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ $	t Nitrogen	C <sub>2</sub> H <sub>2</sub> 15/- 27/-11 38/-36 38/36 18/- 22/- 0/- 22/- 0/- 25/-39 25/-39 25/-39 31/-14	$\begin{array}{r} \hline C_{3}H_{4} \\ \hline -12/- \\ -10/- \\ -20/-23 \\ -20/-23 \\ -20/-19 \\ -23/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -12/-29 \\ -12/-29 \\ -12/-29 \\ 40/88 \\ \end{array}$	$\begin{array}{c} -C_4H_6\\ \hline -/-\\ -22/-12\\ -52/-43\\ -52/-43\\ 16/11\\ -/-\\ -18/-\\ 27/-\\ -27/-\\ -/-\\ -/-\\ -/-\\ -50/-52\\ -50/-52\\ -/-\\ -/-\\ -/-\\ -37/-25 \end{array}$	$\begin{array}{c} \\ -21/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ 26/- \\ 26/- \\ 26/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\39/- \end{array}$	H2 	
no 1 2 3 4 5 7 8 9 10 13 14 15 16 17 18 29 300	reactions DMPyrrole → DMPyrrole(R1) + H• DMPyrrole → DMPyrrole(R2) + H• DMPyrrole → MPyrrole(R2) + H• DMPyrrole → MPyrrole(R1) + CH <sub>3</sub> • DMPyrrole + H• → DMPyrrole(R1) + H2 DMPyrrole + CH <sub>3</sub> • → DMPyrrole(R1) + CD DMPyrrole + CH <sub>3</sub> • → DMPyrrole(R2) + CC DMPyrrole + H• → 2-MPyrrole + CH <sub>3</sub> • DMPyrrole(R1) → C <sub>3</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>4</sub> CN• DMPyrrole(R1) → C <sub>3</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>4</sub> CN• DMPyrrole(R1) → HCN + C <sub>4</sub> H <sub>5</sub> • MPyrrole(R1) → C <sub>3</sub> H <sub>4</sub> + CH <sub>2</sub> CN• MPyrrole(R1) → C <sub>3</sub> H <sub>4</sub> + CH <sub>2</sub> CN• MPyrrole(R1) → C <sub>3</sub> H <sub>4</sub> + CH <sub>2</sub> CN• MPyrrole(R1) → C <sub>3</sub> H <sub>4</sub> + CH <sub>2</sub> CN• MPyrrole(R1) → C <sub>3</sub> H <sub>4</sub> + CH <sub>2</sub> CN• MPyrrole(R1) → S-Picoline + H• DMPyrrole(R2) → 2-Picoline + H•	$\begin{array}{c} CF \\ \hline \\ -/- \\ -10/ \\ -25/ \\ -25/ \\ -25/ \\ -710 \\ H_4 \\ -35/ \\ H_4 \\ -39/ \\ -10$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c} \text{Lucts without} \\ \text{H}_4 & \text{C}_7 \\ \hline & -/- \\ -37 & -41 \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ 12/- \\ -13 \\ -/- \\ -/$	t Nitrogen	C <sub>2</sub> H <sub>2</sub> 15/- 27/-11 38/-36 38/36 18/- 22/- 0/- 22/- 0/- 25/-39 25/-39 31/-14 39/-18	$\begin{array}{r} \hline C_{3}H_{4} \\ \hline -12/- \\ -10/- \\ -20/-23 \\ -20/-23 \\ -20/-19 \\ -23/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -12/-29 \\ -12/-29 \\ 40/88 \\ 67/120 \\ \hline \end{array}$	$\begin{array}{c} -C_4H_6\\ \hline -/-\\ -22/-12\\ -52/-43\\ -52/-43\\ 16/11\\ -/-\\ -18/-\\ 27/-\\ -27/-\\ -/-\\ -27/-\\ -/-\\ -50/-52\\ -50/-52\\ -/-\\ -/-\\ -37/-25\\ -50/-31\\ + 25\\ -50/-32\\ + 25\\ -50/-32\\ + 25\\ -50/-32\\ + 25\\ -50/-32\\ + 25\\ -50/-32\\ + 25\\ -50/-32\\ + 25\\ -50/-32\\ + 25\\ -50/-32\\ + 25\\ -50/-32\\ + 25\\ -50/-32\\ + 25\\ -50/-22\\ + 25\\ -50/-22\\ + 25\\ -50/-$	$\begin{array}{c}2 \\ -21/- \\ -52/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ 26/- \\ 26/- \\ 26/- \\ 26/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -/- \\ -50/- \\ -/- \\ -/- \\ -50/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	H2 -42 -42 -42 	
no 1 2 3 4 5 7 8 9 10 13 14 15 16 17 18 29 30 33 4	reactions DMPyrrole → DMPyrrole(R1) + H* DMPyrrole → DMPyrrole(R2) + H* DMPyrrole → MPyrrole(R1) + CH <sub>3</sub> * DMPyrrole → MPyrrole(R1) + CH <sub>3</sub> * DMPyrrole + H* → DMPyrrole(R1) + H2 DMPyrrole + CH <sub>3</sub> * → DMPyrrole(R1) + CD DMPyrrole + CH <sub>3</sub> * → DMPyrrole(R2) + CC DMPyrrole + H* → 2-MPyrrole + CH <sub>3</sub> * DMPyrrole(R1) → C <sub>3</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>4</sub> CN* DMPyrrole(R1) → C <sub>3</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>4</sub> CN* DMPyrrole(R1) → HCN + C <sub>4</sub> H <sub>5</sub> * MPyrrole(R1) → C <sub>3</sub> H <sub>4</sub> + CH <sub>2</sub> CN* MPyrrole(R1) → C <sub>3</sub> H <sub>4</sub> + CH <sub>2</sub> CN* MPyrrole(R1) → C <sub>3</sub> H <sub>4</sub> + CH <sub>2</sub> CN* DMPyrrole(R1) → C <sub>3</sub> H <sub>4</sub> + CH <sub>2</sub> CN* DMPyrrole(R1) → 5-Picoline + H* DMPyrrole(R2) → 2-Picoline + H* MPyrrole(R3) → Pyridine + H*	$\begin{array}{c} CF \\ \hline \\ -/- \\ -10/ \\ -25/ \\ -25/ \\ -25/ \\ -710 \\ H_4 \\ -35/ \\ H_4 \\ -39/ \\ -10$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c} \text{Lucts without} \\ \text{H}_4 & \text{C}_1 \\ \hline & -/- \\ -& -/- \\ -& -/- \\ 16/- \\ 12/- \\ -& -13 \\ -& -13 \\ -& -13 \\ -& -13 \\ -& -13 \\ -& -13 \\ -& -14 \\ -& -12 \\ -& -/- \\ -& -/$	t Nitrogen 2H6	C <sub>2</sub> H <sub>2</sub> 15/- 27/-11 38/-36 38/36 18/- 22/- 0/- 22/- 22/- 22/- 22/- 22/- 22/- 31/-14 39/-18 - 20	$\begin{array}{r} \hline C_{3}H_{4} \\ \hline -12/- \\ -10/- \\ -20/-23 \\ -20/-23 \\ -20/-19 \\ -23/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -12/-29 \\ -12/-29 \\ 40/88 \\ 67/120 \\ -/11 \\ /11 \\ \end{array}$	$\begin{array}{c} -C_4H_6\\ \hline -/-\\ -22/-12\\ -52/-43\\ -52/-43\\ 16/11\\ -/-\\ -18/-\\ 27/-\\ -27/-\\ -/-\\ -/-\\ -50/-52\\ -50/-52\\ -/-\\ -/-\\ -37/-25\\ -50/-31\\ -/-21\\ /-21\\ \end{array}$	$\begin{array}{c}2 \\ -21/- \\ -52/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ 26/- \\ 26/- \\ 26/- \\ 26/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\26 \\ -/- \\26 \\ -/- \\ -/- \\26 \\ -/- \\ -/- \\ 26/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ 26/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ 26/- \\ -/- \\ -/- \\ -/- \\ -/- \\ 26/- \\ -/ \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	H2 -42 -42 -42 	
no 1 2 3 4 5 7 8 9 10 13 14 15 16 17 18 29 30 33 4 37	$reactions$ $DMPyrrole → DMPyrrole(R1) + H^{\bullet}$ $DMPyrrole → DMPyrrole(R2) + H^{\bullet}$ $DMPyrrole → MPyrrole(R1) + CH_{3}^{\bullet}$ $DMPyrrole → MPyrrole(R2) + CH_{3}^{\bullet}$ $DMPyrrole + H^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R1) + CL_{3}^{\bullet}$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R2) + CL_{3}^{\bullet}$ $DMPyrrole + H → 2 - MPyrrole + CH_{3}^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $MPyrrole(R1) → HCN + C_{4}H_{5}^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → 5 - Picoline + H^{\bullet}$ $MPyrrole(R2) → 2 - Picoline + H^{\bullet}$ $MPyrrole(R4) → Pyridine + H^{\bullet}$	$\begin{array}{c} \hline \\ \hline \\ -/- \\ -10/ \\ -25/ \\ -25/ \\ -25/ \\ -710 \\ \hline \\ H_4 \\ -39/ \\ -10/ \\$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c} \text{hucts without} \\ \text{H}_4 & \text{C}_1 \\ \hline & -/- \\ - & -/- \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ 12/- \\ - & -13 \\ \\ -13 \\ \\ -13 \\ \\ -14 \\ -12 \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -14 \\ -12 \\ -17 \\ -18 \\ 4 \\ -/- \\ 4 \\ -/- \\ 4 \\ -/- \\ -/ \\ -/- \\ -/- \\ -/- \\ -/- \\ -/$	t Nitrogen	$\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline \\ 18/- \\ 22/- \\ 0/- \\ 22/- \\ 0/- \\ 22/- \\ 22/- \\ 31/-14 \\ 39/-18 \\ -20 \\ -20 \\ 30 \\ \end{array}$	$\begin{array}{r} \hline C_{3}H_{4} \\ \hline -12/- \\ -10/- \\ -20/-23 \\ -20/-23 \\ -20/-19 \\ -23/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -12/-29 \\ -12/-29 \\ -12/-29 \\ 40/88 \\ 67/120 \\ -/11 \\ -/11 \\ -/11 \\ -/11 \\ -/- \\ -/ \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	$\begin{array}{c}\\ -22/-12\\ -52/-43\\ -52/-43\\ 16/11\\ -/-\\ -18/-\\ 27/-\\ -27/-\\ -/-\\ -50/-52\\ -50/-52\\ -/-\\ -/-\\ -37/-25\\ -50/-31\\ -/-21\\ -/-21\\ -/43\\ \end{array}$	$\begin{array}{c}2 \\ -21/-\\ -52/-\\ -52/-\\ -52/-\\ 16/10 \\ -/-\\ -18/-\\ 26/-\\ 26/-\\ 26/-\\ -/-\\ -50/-\\ -/-\\ -50/-\\ -/-\\ -39/-\\ -50/-\\ -/-26 \\ -/-26 \\ -/-26 \\ -/-26 \\ -/-26 \\ -/-26 \\ -/-26 \end{array}$	H2 -42 -42 -42 	
no 1 2 3 4 5 7 8 9 10 13 14 15 16 17 18 29 30 33 34 37 38	$reactions$ $DMPyrrole → DMPyrrole(R1) + H^{\bullet}$ $DMPyrrole → DMPyrrole(R2) + H^{\bullet}$ $DMPyrrole → MPyrrole(R1) + CH_{3}^{\bullet}$ $DMPyrrole → MPyrrole(R2) + CH_{3}^{\bullet}$ $DMPyrrole + H^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R1) + C$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R2) + C$ $DMPyrrole + H → 2 - MPyrrole + CH_{3}^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $MPyrrole(R2) → C_{3}H_{4} + C_{4}H_{5}^{\bullet}$ $MPyrrole(R1) → HCN + C_{4}H_{5}^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → 5 - Picoline + H^{\bullet}$ $MPyrrole(R3) → Pyridine + H^{\bullet}$ $MPyrrole(R4) → Pyridine + H^{\bullet}$ $MPyrrole(R1) + H^{\bullet} \rightarrow 4 - MPyrrole$	$\begin{tabular}{ c c c c c } \hline CF \\ \hline -/- \\ -10/- \\ -25/- \\ -25/- \\ -25/- \\ -25/- \\ -10/- \\ -10/- \\ -10/- \\ -10/- \\ -10/- \\ -10/- \\ -10/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c} \text{lucts without} \\ \text{H}_4 & \text{C}_7 \\ \hline & -/- \\ -37 & -41 \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ 12/- \\ -13 \\ -/- \\ -13 \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	t Nitrogen	$\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline \\ 18/- \\ 22/- \\ 0/- \\ 22/- \\ 0/- \\ 22/- \\ 25/-39 \\ 25/-39 \\ 25/-39 \\ 31/-14 \\ 39/-18 \\ -20 \\ -20 \\ -20 \\ 30 \\ 30 \\ \end{array}$	$\begin{array}{r} \hline C_{3}H_{4} \\ \hline -12/- \\ -10/- \\ -20/-23 \\ -20/-23 \\ -20/-19 \\ -23/- \\ -/ \\ -/- \\ -/ \\ -/ \\ -/ \\ -/$	$\begin{array}{c} -C_4H_6\\ \hline -/-\\ -22/-12\\ -52/-43\\ -52/-43\\ 16/11\\ -/-\\ -18/-\\ 27/-\\ -27/-\\ -/-\\ -/-\\ -50/-52\\ -50/-52\\ -/-\\ -/-\\ -37/-25\\ -50/-31\\ -/-21\\ -/43\\ -/43\\ \end{array}$	$\begin{array}{c} \hline C_4 \\ \hline -/- \\ -21/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ -18/- \\ 26/- \\ 26/- \\ 26/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ 26/ \\ 26/ \\ 26/$	H2 -42 -42 -42 	
no 1 2 3 4 5 7 8 9 10 13 14 15 166 177 18 29 30 33 34 37 38 43	$reactions$ $DMPyrrole → DMPyrrole(R1) + H^{\bullet}$ $DMPyrrole → DMPyrrole(R2) + H^{\bullet}$ $DMPyrrole → MPyrrole(R1) + CH_{3}^{\bullet}$ $DMPyrrole → MPyrrole(R2) + CH_{3}^{\bullet}$ $DMPyrrole + H^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R2) + C$ $DMPyrrole + H → 2 - MPyrrole + CH_{3}^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $MPyrrole(R1) → HCN + C_{4}H_{5}^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → 5 - Picoline + H^{\bullet}$ $MPyrrole(R3) → Pyridine + H^{\bullet}$ $MPyrrole(R1) + H^{\bullet} - 4 - MPyrrole$ $MPyrrole(R1) + H^{\bullet} - 4 - MPyrrole$ $MPyrrole(R1) + H^{\bullet} - 4 - MPyrrole$ $MPyrrole(R2) + H^{\bullet} - 2 - MPyrrole$ $MPyrrole(R2) + H^{\bullet} - 4 - MPyrrole(R3) + CH_{3}^{\bullet}$	$\begin{array}{c} CF \\ \hline \\ -/- \\ -10/ \\ -25/ \\ -25/ \\ -25/ \\ -35/ \\ H_4 & -39/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ 12/ \\ -/-12 \\ -/-11 \\ -/-12 \\ -/-11 \\ -/- \\ -/- \\ -/- \\ -/- \\ -/-32 \\ $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c} \text{lucts without} \\ \text{H}_4 & \text{C}_7 \\ \hline & -/- \\ -37 & -41 \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ 12/- \\ -13 \\13 \\13 \\13 \\ -/- \\ -/ \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	t Nitrogen 2H6	$\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline \\ 18/- \\ 22/- \\ 0/- \\ 22/- \\ 0/- \\ 29/- \\ 25/-39 \\ 25/-39 \\ 25/-39 \\ 31/-14 \\ 39/-18 \\ -20 \\ -20 \\ -20 \\ 30 \\ 30 \\ -15 \\ \end{array}$	$\begin{array}{r} \hline C_{3}H_{4} \\ \hline -12/- \\ -10/- \\ -20/-23 \\ -20/-23 \\ -20/-19 \\ -23/- \\ -/ \\ -/- \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	$\begin{array}{c} -C_4H_6\\ \hline -/-\\ -22/-12\\ -52/-43\\ -52/-43\\ 16/11\\ -/-\\ -18/-\\ 27/-\\ -27/-\\ -/-\\ -/-\\ -/-\\ -50/-52\\ -/-\\ -/-\\ -37/-25\\ -50/-51\\ -/-21\\ -/-21\\ -/43\\ -/43\\ -/-12\\ \end{array}$	$\begin{array}{c} \hline C_4 \\ \hline -/- \\ -52/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ -/- \\ 26/- \\ 26/- \\ 26/- \\ 26/- \\ -/ \\ -/- \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	H2 -42 -42 -42 -42 	$\begin{array}{c} \hline C_4H_4 \\ \hline \\ $
no 1 2 3 4 5 7 8 9 10 13 14 15 16 17 18 29 30 33 34 37 38 43 44	$reactions$ $DMPyrrole → DMPyrrole(R1) + H^{\bullet}$ $DMPyrrole → DMPyrrole(R2) + H^{\bullet}$ $DMPyrrole → MPyrrole(R1) + CH_{3}^{\bullet}$ $DMPyrrole → MPyrrole(R2) + CH_{3}^{\bullet}$ $DMPyrrole + H^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R1) + CL_{3}^{\bullet}$ $DMPyrrole + H → 2 - MPyrrole + CH_{3}^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $DMPyrrole(R1) → HCN + C_{4}H_{5}^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → CSH_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → 5 - Picoline + H^{\bullet}$ $MPyrrole(R2) → 2 - Picoline + H^{\bullet}$ $MPyrrole(R3) → Pyridine + H^{\bullet}$ $MPyrrole(R4) → Pyridine + H^{\bullet}$ $MPyrrole(R4) + Pyridine + H^{\bullet}$ $MPyrrole(R4) + Pyridine + H^{\bullet}$ $MPyrrole(R2) + H^{\bullet} → 2 - MPyrrole$ $2 - MPyrrole + CH_{3}^{\bullet} → MPyrrole(R3) + CH_{3}^{\bullet} + MPyrrole(R3) + CH_{3}^{\bullet} + MPyrrole(R4) + CH_{3}^{\bullet} + MPyrrole(R4) + CH_{3}^{\bullet} + MPyrrole(R4) + Pyrrole(R4) + CH_{3}^{\bullet} + MPyrrole(R4) + CH_{3}^{\bullet} + CH_{3}^{\bullet} + MPyrrole(R4) + CH_{3}^{\bullet} + MPyrrole(R4) + CH_{3}^{\bullet} + CH_{3}^{\bullet} + MPyrrole(R4) + CH_{3}^{\bullet} + CH_{3}^{\bullet} + CH_{3}^{\bullet}$	$\begin{tabular}{ c c c c c } \hline CF \\ \hline -/- \\ -10/- \\ -25/- \\ -25/- \\ -25/- \\ -10/- \\ -10/- \\ -10/- \\ -10/- \\ -10/- \\ -10/- \\ -10/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c} \text{lucts without} \\ \text{H}_4 & \text{C}_1 \\ \hline & -/- \\ - & -/- \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ 12/- \\ -13 \\ -/- \\ -13 \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ $	t Nitrogen	$\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline \\ 18/- \\ 22/- \\ 0/- \\ 22/- \\ 0/- \\ 22/- \\ 0/- \\ 29/- \\ 25/-39 \\ 25/$	$\begin{array}{r} \hline C_{3}H_{4} \\ \hline -12/- \\ -10/- \\ -20/-23 \\ -20/-23 \\ -20/-19 \\ -23/- \\ -/- \end{array}$	$\begin{array}{c}\\ -22/-12\\ -52/-43\\ -52/-43\\ 16/11\\ -/-\\ -18/-\\ 27/-\\ -27/-\\ -/-\\ -/-\\ -50/-52\\ -50/-52\\ -/-\\ -/-\\ -37/-25\\ -50/-31\\ -/-21\\ -/43\\ -/-12\\ -/43\\ -/-12\\ -/-$	$\begin{array}{c}2 \\ -21/-\\ -52/-\\ -52/-\\ -52/-\\ 16/10 \\ -/-\\ -26/-\\ 26/-\\ 26/-\\ -/-\\ -50/-\\ -/-\\ -50/-\\ -/-\\ -50/-\\ -/-\\ -39/-\\ -50/-\\ -/-26 \\ -/-26 \\ -/-26 \\ -/-26 \\ -/-26 \\ -/-21 \\ -/-14 \\ -/-14 \\ -/-14 \end{array}$	H2 -42 -42 -42 	$\begin{array}{c} \hline C_4H_4 \\ \hline \\ $
no 1 2 3 4 5 7 8 9 10 13 14 15 16 17 18 29 30 33 34 37 38 43 44 45 5 5 10 10 10 10 10 10 10 10 10 10	$reactions$ $DMPyrrole → DMPyrrole(R1) + H^{\bullet}$ $DMPyrrole → DMPyrrole(R2) + H^{\bullet}$ $DMPyrrole → MPyrrole(R1) + CH_{3}^{\bullet}$ $DMPyrrole → MPyrrole(R2) + CH_{3}^{\bullet}$ $DMPyrrole + H^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R1) + C$ $DMPyrrole + H^{\bullet} → 2-MPyrrole + CH_{3}^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $DMPyrrole(R1) → HCN + C_{4}H_{5}^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → CSH_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → 5-Picoline + H^{\bullet}$ $MPyrrole(R2) → 2-Picoline + H^{\bullet}$ $MPyrrole(R3) → Pyridine + H^{\bullet}$ $MPyrrole(R4) → Pyridine + H^{\bullet}$ $MPyrrole(R4) + Pyridine + H^{\bullet}$ $MPyrrole(R1) + H^{\bullet} → 2-MPyrrole$ $2-MPyrrole(R2) + H^{\bullet} → 2-MPyrrole$ $2-MPyrrole(R3) + H^{\bullet} → 2-MPyrrole$ $2-MPyrrole(R4) + H^{\bullet} → 2-MPyrrole$ $3-MPyrrole(R4) + H^{\bullet} → MPyrrole(R4) + CH^{\bullet} →$	$\begin{array}{c} CF \\ \hline \\ -/- \\ -10/ \\ -25/ \\ -25/ \\ -25/ \\ -25/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c} \text{lucts without} \\ \text{H}_4 & \text{C}_1 \\ \hline & -/- \\ - & -/- \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ 12/- \\ -13 \\13 \\13 \\ -/- \\ -/ \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -$	t Nitrogen	$\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline \\ 18/- \\ 22/- \\ 0/- \\ 22/- \\ 0/- \\ 29/- \\ 25/-39 \\ 25/-39 \\ 25/-39 \\ 25/-39 \\ 31/-14 \\ 39/-18 \\ -20 \\ -20 \\ -20 \\ 30 \\ 30 \\ -15 \\ -15 \\ -15 \\ 50/-78 \\ \end{array}$	$\frac{C_{3}H_{4}}{-12/-}$ $-10/-$ $-20/-23$ $-20/-23$ $-20/-19$ $-23/-$ $-/-$	$\begin{array}{c} C_4H_6 \\ \hline -/- \\ -22/-12 \\ -52/-43 \\ -52/-43 \\ 16/11 \\ -/- \\ -18/- \\ 27/- \\ -27/- \\ -/- \\ -/- \\ -50/-52 \\ -/- \\ -/- \\ -50/-52 \\ -/- \\ -/- \\ -37/-25 \\ -50/-31 \\ -/-21 \\ -/43 \\ -/-12 \\ -/43 \\ -/-12 \\ -/-12 \\ 214/1107 \\ -20/-12 \\ -/-1$	$\begin{array}{c} \hline C_4 \\ \hline \\ -/2 \\ -52/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ -18/- \\ 26/- \\ 26/- \\ 26/- \\ -/- \\ -/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -39/- \\ -50/- \\ -/- \\ 26 \\ -/-26 \\ -$	H2 -42 -42 -42 	$\begin{array}{c} \hline C_4H_4 \\ \hline \\ \hline \\ -48/-43 \\ \hline \\ -48/-43 \\ \hline \\ -48/-43 \\ \hline \\ -49/-46 \\ \hline \\ -100/-99 \\ \hline \\ \\ 11 \\ 13 \\ -100/-99 \\ \end{array}$
no 1 2 3 4 5 7 8 9 10 13 14 15 16 17 18 29 30 33 34 37 38 43 44 45 46 17 18 29 30 33 34 45 17 18 29 30 33 34 45 17 18 29 30 33 34 45 17 18 29 30 33 34 45 17 18 29 30 33 34 45 17 18 29 30 33 34 45 17 18 29 30 33 34 45 17 18 29 30 33 34 45 16 17 18 29 30 33 34 45 16 17 18 18 19 19 10 10 10 10 10 10 10 10 10 10	$reactions$ $DMPyrrole → DMPyrrole(R1) + H^{\bullet}$ $DMPyrrole → DMPyrrole(R2) + H^{\bullet}$ $DMPyrrole → MPyrrole(R1) + CH_{3}^{\bullet}$ $DMPyrrole → MPyrrole(R2) + CH_{3}^{\bullet}$ $DMPyrrole + H^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R1) + C$ $DMPyrrole + H^{\bullet} → 2-MPyrrole + CH_{3}^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $DMPyrrole(R1) → HCN + C_{4}H_{5}^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → 5-Picoline + H^{\bullet}$ $MPyrrole(R2) → 2-Picoline + H^{\bullet}$ $MPyrrole(R3) → Pyridine + H^{\bullet}$ $MPyrrole(R4) → Pyridine + H^{\bullet}$ $MPyrrole(R1) + H^{\bullet} → 4-MPyrrole$ $2-MPyrrole(R2) + H^{\bullet} → 2-MPyrrole$ $2-MPyrrole(R2) + H^{\bullet} → 2-MPyrrole$ $2-MPyrrole(R4) + Pyridine + H^{\bullet}$ $MPyrrole(R4) + H^{\bullet} → 2-MPyrrole$ $2-MPyrrole(R4) + H^{\bullet} → 2-MPyrrole$ $2-MPyrrole(R4) + H^{\bullet} → 2-MPyrrole$ $2-MPyrrole(R4) + H^{\bullet} → 2-MPyrrole(R4) + CH_{4}$ $4-MPyrrole(R4) + H^{\bullet} → 2-MPyrrole(R4) + CH_{4}$ $4-MPyrrole(R4) + H^{\bullet}$ $4-MPyrrole(R4) + H^{\bullet} → 2-MPyrrole(R4) + CH_{4}$ $4-MPyrrole(R4) + H^{\bullet}$ $4-MPyrrole(R4) +$	$\begin{array}{c} CF \\ \hline \\ -/- \\ -10/ \\ -25/ \\ -25/ \\ -25/ \\ -710 \\ H_4 \\ -39/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -/- \\ -/ \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c} \text{lucts withou} \\ \text{H}_4 & \text{C}_1 \\ \hline & -/- \\ - & -/- \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ 12/- \\ -13 \\ -/- \\ -13 \\ -/- \\$	t Nitrogen	$\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline \\ 18/- \\ 22/- \\ 0/- \\ 22/- \\ 0/- \\ 29/- \\ 25/-39 \\ 25/-39 \\ 25/-39 \\ 25/-39 \\ 31/-14 \\ 39/-18 \\ -20 \\ -20 \\ -20 \\ 30 \\ 30 \\ -15 \\ -15 \\ -15 \\ 50/-78 \\ \end{array}$	$\frac{C_{3}H_{4}}{-12/-}$ $-10/-$ $-20/-23$ $-20/-23$ $-20/-19$ $-23/-$ $-/-$	$\begin{array}{c} C_4H_6 \\ \hline -/- \\ -22/-12 \\ -52/-43 \\ -52/-43 \\ 16/11 \\ -/- \\ -18/- \\ 27/- \\ -27/- \\ -/- \\ -/- \\ -50/-52 \\ -50/-52 \\ -/- \\ -/- \\ -37/-25 \\ -50/-31 \\ -/-21 \\ -/43 \\ -/-21 \\ -/43 \\ -/-12 \\ -/-12 \\ 214/1107 \\ -100/-100 \\ -/-01 \\ -/-00 $	$\begin{array}{c} \hline C_4 \\ \hline \\ -/2 \\ -21/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ -18/- \\ 26/- \\ 26/- \\ 26/- \\ -/ \\ -/- \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	H2 -42 -42 -42 	$\begin{array}{c} \hline C_4H_4 \\ \hline \\ \hline \\ -48/-43 \\ \hline \\ -48/-43 \\ \hline \\ -48/-43 \\ \hline \\ -49/-46 \\ \hline \\ -49/-40 \\ \hline \\ -40/-40 \\ \hline \\ -40/$
no 1 2 3 4 5 7 8 9 10 13 14 5 7 8 9 10 13 14 15 16 17 18 29 30 33 34 37 38 43 44 5 7 8 9 10 13 14 15 16 17 18 29 30 33 34 45 17 18 29 30 33 34 45 17 18 29 30 33 34 45 17 18 29 30 33 34 45 17 18 29 30 33 34 45 17 18 29 30 33 34 45 16 17 18 29 30 33 34 45 16 17 18 18 19 19 10 10 10 10 10 10 10 10 10 10	$reactions$ $DMPyrrole → DMPyrrole(R1) + H^{\bullet}$ $DMPyrrole → DMPyrrole(R2) + H^{\bullet}$ $DMPyrrole → MPyrrole(R1) + CH_{3}^{\bullet}$ $DMPyrrole → MPyrrole(R2) + CH_{3}^{\bullet}$ $DMPyrrole + H^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R1) + C$ $DMPyrrole + H^{\bullet} → 2-MPyrrole + CH_{3}^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $MPyrrole(R1) → HCN + C_{4}H_{5}^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → 5-Picoline + H^{\bullet}$ $MPyrrole(R2) → 2-Picoline + H^{\bullet}$ $MPyrrole(R3) → Pyridine + H^{\bullet}$ $MPyrrole(R1) + H^{\bullet} → 4-MPyrrole$ $MPyrrole(R2) + H^{\bullet} → 2-MPyrrole$ $2-MPyrrole(R2) + H^{\bullet} → 2-MPyrrole$ $2-MPyrrole(R2) + H^{\bullet} → 2-MPyrrole$ $4-MPyrrole(R3) + H^{\bullet} → CH_{3}^{\bullet} + CH_{3}^{\bullet}$ $MPyrrole(R4) + H^{\bullet}$ $C_{4}H_{5}^{\bullet} + C_{4}H_{4} + H^{\bullet}$ $C_{4}H_{5}^{\bullet} + C_{4}H_{2} + H^{\bullet}$ $C_{4}H_{5}^{\bullet} + H^{\bullet} - C_{4}H_{5}$ $C_{4}H_{5}^{\bullet} + H^{\bullet} - C_{4}H_{5}$	$\begin{array}{c} CF \\ \hline \\ -/- \\ -10/ \\ -25/ \\ -25/ \\ -25/ \\ -25/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -/- \\ -/ \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c} \text{lucts without} \\ \text{H}_4 & \text{C}_1 \\ \hline & -/- \\ - & -/- \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ 12/- \\ -13 \\13 \\13 \\13 \\ -/- \\ -/ \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ $	t Nitrogen	$\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline \\ 18/- \\ 22/- \\ 0/- \\ 22/- \\ 0/- \\ 29/- \\ 25/-39 \\ 25/-39 \\ 25/-39 \\ 25/-39 \\ 31/-14 \\ 39/-18 \\ -20 \\ -20 \\ -20 \\ 30 \\ 30 \\ -15 \\ -15 \\ 50/-78 \\ \hline \\ \end{array}$	$\frac{C_{3}H_{4}}{-12/-}$ $-10/-$ $-20/-23$ $-20/-23$ $-20/-19$ $-23/-$ $-/-$	$\begin{array}{c}\\ -22/-12\\ -52/-43\\ -52/-43\\ 16/11\\ -/-\\ -18/-\\ 27/-\\ -27/-\\ -/-\\ -/-\\ -50/-52\\ -50/-52\\ -/-\\ -/-\\ -37/-25\\ -50/-31\\ -/-21\\ -/43\\ -/-12\\ -/43\\ -/-12\\ 214/1107\\ -100/-100\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -$	$\begin{array}{c} \hline C_4 \\ \hline -/- \\ -21/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ -18/- \\ 26/- \\ 26/- \\ 26/- \\ -/ \\ -/- \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	H2 -42 -42 -42 -42 	$\begin{array}{c} \hline C_4H_4 \\ \hline \\ $
no 1 2 3 4 5 7 8 9 10 13 14 5 7 8 9 10 13 14 15 16 17 18 29 30 33 34 37 38 43 44 45 5 6 6 17 18 29 30 33 34 45 5 7 8 9 10 13 14 15 16 17 18 29 30 33 34 45 17 18 29 30 33 34 45 16 17 18 29 30 33 34 45 16 17 18 29 30 33 34 45 16 17 18 29 30 33 34 45 16 17 18 29 30 33 34 45 16 17 18 29 30 33 34 45 16 17 18 29 30 33 34 45 16 17 18 29 30 30 33 14 15 16 17 18 29 30 33 34 45 16 17 18 29 30 35 10 10 10 10 10 10 10 10 10 10	$reactions$ $DMPyrrole → DMPyrrole(R1) + H^{\bullet}$ $DMPyrrole → DMPyrrole(R2) + H^{\bullet}$ $DMPyrrole → MPyrrole(R1) + CH_{3}^{\bullet}$ $DMPyrrole → MPyrrole(R2) + CH_{3}^{\bullet}$ $DMPyrrole + H^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R2) + C$ $DMPyrrole + H^{\bullet} → 2-MPyrrole + CH_{3}^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $MPyrrole(R1) → HCN + C_{4}H_{5}^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → 5-Picoline + H^{\bullet}$ $MPyrrole(R2) → 2-Picoline + H^{\bullet}$ $MPyrrole(R1) + H^{\bullet} \rightarrow 4-MPyrrole$ $MPyrrole(R2) + H^{\bullet} 2-MPyrrole$ $MPyrrole(R2) + H^{\bullet} + 2-MPyrrole$ $MPyrrole(R2) + H^{\bullet} + 2-MPyrrole$ $MPyrrole(R3) + Pyridine + H^{\bullet}$ $MPyrrole(R1) + H^{\bullet} \rightarrow 4-MPyrrole$ $MPyrrole(R3) + CH_{3}^{\bullet} \rightarrow MPyrrole(R3) + CH_{4}^{\bullet}$ $MPyrrole(R4) + Pyriole(R4) + CH_{4}^{\bullet}$ $MPyrrole(R4) + H^{\bullet} + 4-MPyrrole(R4) + CH_{4}^{\bullet}$ $MPyrrole(R4) + H^{\bullet}$ $MPyrrole(R4)$	$\begin{array}{c} CF \\ \hline \\ -/- \\ -10/ \\ -25/ \\ -25/ \\ -25/ \\ -25/ \\ -3/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -10/ \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ 12/ \\ -/-12 \\ -/-12 \\ -/-12 \\ -/-12 \\ -/-12 \\ -/-12 \\ -/-12 \\ -/-12 \\ -/-12 \\ -/-12 \\ -/-12 \\ -/-12 \\ -/-10 \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c} \text{lucts withou} \\ \text{H}_4 & \text{C}_1 \\ \hline & -/- \\ - & -/- \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ 12/- \\ -13 \\ -/- \\ -/3 \\ -/- \\ -/ \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- $	t Nitrogen	$\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline \\ 18/- \\ 22/- \\ 0/- \\ 22/- \\ 0/- \\ 29/- \\ 25/-39 \\ 25/-39 \\ 25/-39 \\ 25/-39 \\ 31/-14 \\ 39/-18 \\ -20 \\ -20 \\ -20 \\ -30 \\ -15 \\ -15 \\ -15 \\ 50/-78 \\ \hline \\ 0 \\ -15 \\ -1$	$\frac{C_{3}H_{4}}{-12/-}$ $-10/-$ $-20/-23$ $-20/-23$ $-20/-19$ $-23/-$ $-/-$	$\begin{array}{c} -C_4H_6\\ \hline -/-\\ -22/-12\\ -52/-43\\ -52/-43\\ 16/11\\ -/-\\ -18/-\\ 27/-\\ -27/-\\ -/-\\ -/-\\ -/-\\ -50/-52\\ -/-\\ -/-\\ -37/-25\\ -50/-52\\ -/-\\ -/-\\ -37/-25\\ -50/-31\\ -/-21\\ -/-21\\ -/43\\ -/-12\\ 214/1107\\ -100/-100\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -/-\\ -$	$\begin{array}{c} \hline C_4 \\ \hline \\ -/2 \\ -52/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ -18/- \\ 26/- \\ 26/- \\ 26/- \\ -26 \\ -/- \\ -/ \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/-$	H2 -42 -42 -42 -42 -7 -42 -7 -7 -7 -7 -7 -7 -7 -7 -7 -7 -7 -7 -7	$\begin{array}{c} \hline C_4H_4 \\ \hline \\ \hline \\ 18 \\ -48/-43 \\ \hline \\ -48/-43 \\ \hline \\ -49/-46 \\ \hline \\ -100/-99 \\ \hline \\ -100/-99 \\ \hline \\ -40/-40 \\ \hline \\ \\ -40/-40 \\ \hline \\ -40/-40 \\$
no 1 2 3 4 5 7 8 9 10 13 14 15 166 17 18 29 30 33 34 37 38 43 44 45 50 51 51 51 51 51 51 51 51 51 51	$reactions$ $DMPyrrole → DMPyrrole(R1) + H^{\bullet}$ $DMPyrrole → DMPyrrole(R2) + H^{\bullet}$ $DMPyrrole → MPyrrole(R1) + CH_{3}^{\bullet}$ $DMPyrrole → MPyrrole(R2) + CH_{3}^{\bullet}$ $DMPyrrole + H^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + H^{\bullet} → 2-MPyrrole(R2) + C$ $DMPyrrole + H^{\bullet} → 2-MPyrrole + CH_{3}^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $MPyrrole(R1) → HCN + C_{4}H_{5}^{\bullet}$ $MPyrrole(R1) → HCN + C_{4}H_{5}^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R1) → 5-Picoline + H^{\bullet}$ $MPyrrole(R2) → 2-Picoline + H^{\bullet}$ $MPyrrole(R1) + H^{\bullet} → 4-MPyrrole$ $MPyrrole(R2) + H^{\bullet} → 2-MPyrrole$ $MPyrrole(R2) + H^{\bullet} → 2-MPyrrole$ $MPyrrole(R2) + H^{\bullet} → 2-MPyrrole$ $MPyrrole(R3) + Pyridine + H^{\bullet}$ $MPyrrole(R1) + H^{\bullet} → 4-MPyrrole$ $MPyrrole(R3) + H^{\bullet} → 2-MPyrrole$ $2-MPyrrole + CH_{3}^{\bullet} → MPyrrole(R3) + CH_{4}^{\bullet} + M^{\bullet} → C_{4}H_{6}^{\bullet}$ $C_{4}H_{3}^{\bullet} + H^{\bullet} → C_{4}H_{6}^{\bullet}$ $C_{4}H_{4}^{\bullet} + H^{\bullet} → C_{2}H_{2}^{\bullet} + H_{2}^{\bullet}$ $C_{4}H_{4}^{\bullet} + H^{\bullet} → C_{2}H_{2}^{\bullet} + C_{2}H_{3}^{\bullet}$	$\begin{array}{c} CF \\ \hline -/- \\ -10/- \\ -25/- \\ -25/- \\ -25/- \\ -10/- \\ -10/- \\ -10/- \\ -10/- \\ -10/- \\ -/ \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c} \mbox{lucts without} \\ \mbox{H}_4 & C, \\  & -/-$	t Nitrogen	$\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline \\ 18/- \\ 22/- \\ 0/- \\ 22/- \\ 22/- \\ 22/- \\ 22/- \\ 22/- \\ 22/- \\ 30/-1 \\ 33/-18 \\ -20 \\ -20 \\ -20 \\ 30 \\ -15 \\ -15 \\ 50/-78 \\ 48/-73 \\ \end{array}$	$\begin{array}{c} \hline C_{3}H_{4} \\ \hline -12/- \\ -10/- \\ -20/-23 \\ -20/-23 \\ -20/-19 \\ -23/- \\ -/ \\ -/ \\ -/ \\ -/$	$\begin{array}{c} C_4H_6 \\ \hline -/- \\ -22/-12 \\ -52/-43 \\ -52/-43 \\ 16/11 \\ -/- \\ -18/- \\ 27/- \\ -27/- \\ -/- \\ -50/-52 \\ -/- \\ -/- \\ -50/-52 \\ -/- \\ -/- \\ -37/-25 \\ -50/-31 \\ -/-21 \\ -/-21 \\ -/43 \\ -/-12 \\ 214/1107 \\ -100/-100 \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \end{array}$	$\begin{array}{c} \hline C_4 \\ \hline \\ -/- \\ -21/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ 26/- \\ 26/- \\ 26/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -39/- \\26 \\ -/-$	H2 -42 -42 -42 -42 -42 -7 -7 -7 -7 -7 -7 -7 -7 -7 -7	$\begin{array}{c} \hline C_4H_4 \\ \hline \\ \hline \\ 18 \\ -48/-43 \\ \hline \\ -48/-43 \\ \hline \\ -49/-46 \\ \hline \\ -22 \\ \hline \\ 11 \\ \hline \\ 13 \\ \hline \\ -100/-99 \\ \hline \\ -22 \\ \hline \\ 22 \\ 22 \\ \hline \\ 22 \\ 22 \\ \hline \\ 22 \\ 22 \\ \hline \\ 22 \\ 22 \\ \hline \\ 22 \\ $
$\begin{array}{c} & & & \\$	$\label{eq:reactions} \hline reactions \\ \hline DMPyrrole \rightarrow DMPyrrole(R1) + H^{\bullet} \\ DMPyrrole \rightarrow DMPyrrole(R2) + H^{\bullet} \\ DMPyrrole \rightarrow MPyrrole(R1) + CH_3^{\bullet} \\ DMPyrrole \rightarrow MPyrrole(R1) + CH_3^{\bullet} \\ DMPyrrole + H^{\bullet} \rightarrow DMPyrrole(R1) + H2 \\ DMPyrrole + CH_3^{\bullet} \rightarrow DMPyrrole(R1) + H2 \\ DMPyrrole + CH_3^{\bullet} \rightarrow DMPyrrole(R2) + C \\ DMPyrrole + H^{\bullet} 2 - MPyrrole + CH_3^{\bullet} \\ DMPyrrole(R1) \rightarrow C_3H_4 + C_2H_4CN^{\bullet} \\ DMPyrrole(R1) \rightarrow C_3H_4 + C_2H_4CN^{\bullet} \\ DMPyrrole(R1) \rightarrow C_3H_4 + C_2H_4CN^{\bullet} \\ MPyrrole(R2) \rightarrow C_3H_4 + CH_2CN^{\bullet} \\ MPyrrole(R2) \rightarrow C_3H_4 + CH_2CN^{\bullet} \\ MPyrrole(R2) \rightarrow C_3H_4 + CH_2CN^{\bullet} \\ DMPyrrole(R2) \rightarrow C_3H_4 + CH_2CN^{\bullet} \\ DMPyrrole(R1) \rightarrow 5 - Picoline + H^{\bullet} \\ DMPyrrole(R2) \rightarrow 2 - Picoline + H^{\bullet} \\ MPyrrole(R3) \rightarrow Pyridine + H^{\bullet} \\ MPyrrole(R3) \rightarrow Pyridine + H^{\bullet} \\ MPyrrole(R1) + H^{\bullet} \rightarrow 4 - MPyrrole \\ MPyrrole(R1) + H^{\bullet} \rightarrow 2 - MPyrrole \\ 2 - MPyrrole(R1) + H^{\bullet} \rightarrow 2 - MPyrrole \\ (R4)^{\bullet} - C_4H_4 + H^{\bullet} \\ C_4H_5^{\bullet} \rightarrow C_4H_6 \\ C_4H_5^{\bullet} \rightarrow C_4H_6 \\ C_4H_5^{\bullet} \rightarrow C_4H_5^{\bullet} + H_2 \\ C_4H_4 + H^{\bullet} \rightarrow C_4H_5^{\bullet} \\ C_4H_5 + H^{\bullet} \rightarrow C_4H_5^{\bullet} \\ C_4H_4 + H^{\bullet} \rightarrow C_4H_5^{\bullet} \\ C_3H_4 + H^{\bullet} \rightarrow C_4H_5^{\bullet} \\ C_3H_5^{\bullet} \\ C_3H_5^{\bullet} + C_3H_5^{\bullet} \\ C_3H_5^{\bullet} \\ C_3H_5^{\bullet} + C_3H_5^{\bullet} \\ C_2H_2^{\bullet} \\ C_3H_4^{\bullet} \\ C_3H_5^{\bullet} \\$	$\begin{array}{c} CF \\ \hline -/- \\ -10/- \\ -25/- \\ -25/- \\ -25/- \\ -10/- \\ -39/- \\ -10/- \\ -10/- \\ -10/- \\ -10/- \\ -/ \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c} \mbox{ucts without} \\ \mbox{H}_4 & \ C_1 \\ \ -/- \\ -/- \\ \ -/- \\ \ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ \ -/- \\ -/$	t Nitrogen	$\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline \\ 22/- \\ 22/- \\ 22/- \\ 22/- \\ 22/- \\ 22/- \\ 38/-18 \\ -20 \\ -20 \\ 30 \\ -15 \\ -15 \\ 50/-78 \\ 48/-73 \\ 49/-24 \\ \end{array}$	$\begin{array}{r} \hline C_{3}H_{4} \\ \hline -12/- \\ -10/- \\ -20/-23 \\ -20/-23 \\ -20/-19 \\ -23/- \\ -/ \\ -/- \\ -/ \\ -/ \\ -/ \\ -/$	$\begin{array}{c} C_4H_6 \\ \hline -/- \\ -22/-12 \\ -52/-43 \\ -52/-43 \\ 16/11 \\ -/- \\ -18/- \\ 27/- \\ -27/- \\ -/- \\ -50/-52 \\ -/- \\ -/- \\ -50/-52 \\ -/- \\ -/- \\ -/- \\ -37/-25 \\ -50/-31 \\ -/-21 \\ -/-21 \\ -/43 \\ -/-12 \\ 214/1107 \\ -100/-100 \\ -/- \\ -$	$\begin{array}{c} \hline C_4 \\ \hline \\ -/- \\ -52/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ 26/- \\ 26/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -14 \\ -/-14 \\ -100/ \\ -99/- \\ -99/- \\ -/- \\ -/- \\ -/14 \\ -/- \\ -/ \\ -/- \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	H2 -42 -42 -42 -42 -42 -7 -7 -7 -7 -7 -7 -7 -7 -7 -7	$\begin{array}{c} \hline C_4H_4 \\ \hline \\ \hline \\ 18 \\ -48/-43 \\ \hline \\ -48/-43 \\ \hline \\ -49/-46 \\ \hline \\ -22 \\ \hline \\ 11 \\ \hline \\ 13 \\ -100/-99 \\ \hline \\ -22 \\ \hline $
no 1 2 3 4 5 7 8 9 10 13 4 5 7 8 9 10 13 4 15 16 17 18 29 30 33 34 43 44 45 46 48 9 5 5 7 8 9 10 13 14 15 16 17 18 29 30 33 43 44 5 5 5 5 5 5 5 5 5 5 5 5 5	$reactions$ $DMPyrrole → DMPyrrole(R1) + H^{\bullet}$ $DMPyrrole → DMPyrrole(R2) + H^{\bullet}$ $DMPyrrole → MPyrrole(R1) + CH_{3}^{\bullet}$ $DMPyrrole → MPyrrole(R2) + CH_{3}^{\bullet}$ $DMPyrrole + H^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R2) + C$ $DMPyrrole + H^{\bullet} → 2 - MPyrrole + CH_{3}^{\bullet}$ $DMPyrrole + H^{\bullet} → 2 - MPyrrole + CH_{3}^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + C_{4}H_{4}N^{\bullet}$ $MPyrrole(R2) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R2) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $MPyrrole(R2) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $DMPyrrole(R1) → 5 - Picoline + H^{\bullet}$ $MPyrrole(R2) → 2 - Picoline + H^{\bullet}$ $MPyrrole(R3) → Pyridine + H^{\bullet}$ $MPyrrole(R3) → Pyridine + H^{\bullet}$ $MPyrrole(R1) + H^{\bullet} → 4 - MPyrrole$ $MPyrrole(R1) + H^{\bullet} → 4 - MPyrrole$ $MPyrrole(R2) + H^{\bullet} → 2 - MPyrrole$ $MPyrrole(R4) → Pyridine + H^{\bullet}$ $MPyrrole(R4) → Pyridine + H^{\bullet}$ $MPyrrole(R4) + H^{\bullet} → 4 - MPyrrole$ $(R4) + M^{\bullet} → C_{4}H_{5}$ $C_{4}H_{5} + H^{\bullet} → C_{4}H_{6}$ $C_{4}H_{5} → C_{4}H_{2} + H^{\bullet}$ $C_{4}H_{4} + H^{\bullet} - C_{4}H_{3} + H_{2}$ $C_{4}H_{4} + H^{\bullet} → C_{4}H_{5}$ $C_{3}H_{4} + H^{\bullet} → C_{4}H_{5}$ $C_{3}H_{4} + H^{\bullet} → C_{4}H_{5}$ $C_{3}H_{4} + H^{\bullet} → C_{4}H_{5}$ $C_{4}H_{6} + H^{\bullet} → C_{4}H_{5}$ $C_{3}H_{4} + H^{\bullet} → C_{4}H_{5}$ $C_{3}H_{4} + H^{\bullet} → C_{4}H_{5}$ $C_{4}H_{6} + H^{\bullet} → C_{4}H_{5}$ $C_{3}H_{4} + H^{\bullet} → C_{4}H_{5}$ $C_{4}H_{6} + H^{\bullet} → C_{4}H_{6}$ $C_{4}H_{6} + H^{\bullet} → C_{4}H_{6}$ $C_{4}H_{6} + H^{\bullet} → C_{4}H_{6}$ $C_{4}H_{7} + C_{4}H_{7} + C_{4}H_{7}$ $C_{4}H_{7} + C_{4}H_{7$	$\begin{array}{c} CF \\ \hline -/- \\ -10/- \\ -25/- \\ -25/- \\ -25/- \\ -10/- \\ -35/- \\ -10/- \\ -10/- \\ -10/- \\ -10/- \\ -/ \\ -/- \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	B. Prod           I4 $C_2$ -/-         -/-           -13         -14/           -19         -49/           -10         21/-           -13         -13/           -13         -13/           -13         -13/           -13         -13/           -14/         -/-           -/-	$\begin{array}{c c} \text{lucts without} \\ \text{H}_4 & \text{C}_7 \\ \hline - & -/- \\ -37 & -41 \\ -37 & -41 \\ -37 & -41 \\ -37 & -41 \\ -/- \\ 16/- \\ 12/- \\ -16/- \\ -13 \\ -/- \\13 \\ -/- \\13 \\ -/- \\ -/ \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -$	t Nitrogen	$\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline \\ 18/- \\ 22/- \\ 22/- \\ 22/- \\ 22/- \\ 22/- \\ 38/-18 \\ -20 \\ 25/-39 \\ 25/-39 \\ 25/-39 \\ -20 \\ -20 \\ -20 \\ -20 \\ -20 \\ -30 \\ -15 \\ -15 \\ 50/-78 \\ -15 \\ -15 \\ 50/-78 \\ -48/-73 \\ 49/-24 \\ -24 $	$\frac{C_{3}H_{4}}{-12/-}$ $-10/-$ $-20/-23$ $-20/-23$ $-20/-19$ $-23/-$ $-/-$ $-/-$ $-/-$ $-/-$ $-7/-$ $-7/-$ $-12/-29$ $-12/-29$ $40/88$ $67/120$ $-/11$ $-/11$ $-/-$	$\begin{array}{c} C_4H_6 \\ \hline -/- \\ -22/-12 \\ -52/-43 \\ -52/-43 \\ 16/11 \\ -/- \\ -18/- \\ 27/- \\ -27/- \\ -/- \\ -/- \\ -50/-52 \\ -50/-52 \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ 214/1107 \\ -100/-100 \\ -/- $	$\begin{array}{c} \hline C_4 \\ \hline \\ -/- \\ -52/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ 26/- \\ 26/- \\ 26/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -39/- \\ -/- \\ -39/- \\ -/- \\ 100/ \\ 0 \\ -/- \\ -99/- \\ -99/- \\ -99/- \\ -/- \\ -/- \\ -14 \\ -100/ \\ 0 \\ -/- \\ -99/- \\ -/- \\ -/- \\ -/- \\ -25 \\ -/-$	H2 -42 -42 -42 -42 -42 -7 -7 -7 -7 -7 -7 -7 -7 -7 -7	$\begin{array}{c} \hline C_4H_4 \\ \hline \\ $
no 1 2 3 4 5 7 8 9 10 13 4 5 7 8 9 10 13 14 15 16 17 18 29 30 33 43 44 45 46 48 9 50 51 51 6 6 7 8 9 10 13 14 15 16 17 18 29 30 33 43 44 45 55 56 57 57 57 57 57 57 57 57 57 57	$reactions$ $DMPyrrole → DMPyrrole(R1) + H^{\bullet}$ $DMPyrrole → DMPyrrole(R2) + H^{\bullet}$ $DMPyrrole → MPyrrole(R1) + CH_{3}^{\bullet}$ $DMPyrrole → MPyrrole(R2) + CH_{3}^{\bullet}$ $DMPyrrole + H^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R1) + H2$ $DMPyrrole + CH_{3}^{\bullet} → DMPyrrole(R1) + CL$ $DMPyrrole + H^{\bullet} → 2 - MPyrrole + CH_{3}^{\bullet}$ $DMPyrrole + H^{\bullet} → 2 - MPyrrole + CH_{3}^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $DMPyrrole(R1) → C_{3}H_{4} + C_{2}H_{4}CN^{\bullet}$ $MPyrrole(R1) → C_{3}H_{4} + C_{4}H_{4}N^{\bullet}$ $MPyrrole(R2) → C_{3}H_{4} + CH_{2}CN^{\bullet}$ $DMPyrrole(R1) → 5 - Picoline + H^{\bullet}$ $MPyrrole(R3) → Pyridine + H^{\bullet}$ $MPyrrole(R3) → Pyridine + H^{\bullet}$ $MPyrrole(R2) + H^{\bullet} → 2 - MPyrrole$ $MPyrrole(R1) + H^{\bullet} → 4 - MPyrrole$ $MPyrrole(R1) + H^{\bullet} → 4 - MPyrrole$ $MPyrrole(R1) + H^{\bullet} → 4 - MPyrrole$ $MPyrrole(R2) + H^{\bullet} → 2 - MPyrrole$ $MPyrrole(R4) → Pyridine + H^{\bullet}$ $MPyrrole(R4) + Pyridine + H^{\bullet}$ $MPyrrole(R4) + H^{\bullet} → 2 - MPyrrole$ $MPyrrole(R4) + M^{\bullet} → 2 - MPyrrole$ $MPyrrole(R4) + M^{\bullet} $	$\begin{array}{c} CF \\ \hline -/- \\ -10/- \\ -25/- \\ -25/- \\ -25/- \\ -10/- \\ -10/- \\ -10/- \\ -10/- \\ -10/- \\ -/ \\ -/- \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -$	B. Prod           I4         C21           -/-         -/-           -13         -14/           -19         -49/           -10         21/-           -13         -13/           -13         -13/           -13         -13/           -13         -13/           -14/         -/-           -/- <t< td=""><td>Lucts without           H4         C.           <math>-/ -/ -37</math> <math>-41</math> <math>-37</math> <math>-41</math> <math>-7 -6/ 12/ -13</math> <math>13</math> <math>-/ 13</math> <math>-/ -17</math> <math>-18</math> <math>-17</math> <math>-16</math> <math>-17</math> <math>-18</math> <math>-16</math> <math>-17</math> <math>-17</math> <math>-16</math> <math>-17</math> <math>-16</math> <math>-17</math> <math>-16</math> <math>-17</math> <math>-17</math> <math>-16</math> <math>-17</math> <math>-17</math> <math>-17</math> <math>-17</math> <math>-17</math> <math>-17</math> <math>-17</math> <math>-17</math></td><td>t Nitrogen</td><td><math display="block">\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline \\ 18/- \\ 22/- \\ 22/- \\ 22/- \\ 22/- \\ 38/-18 \\ -20 \\ -20 \\ -20 \\ -20 \\ -20 \\ -30 \\ -15 \\ -15 \\ 50/-78 \\ -15 \\ 50/-78 \\ -48/-73 \\ 49/-24 \\ -24 \\ -24 \\ -27 \\ -24 \\ -27 \\ -24 \\ -27 \\ -24 \\ -27 \\ -2</math></td><td><math display="block">\frac{C_{3}H_{4}}{-12/-}</math> <math display="block">-10/-</math> <math display="block">-20/-23</math> <math display="block">-20/-23</math> <math display="block">-20/-19</math> <math display="block">-23/-</math> <math display="block">-/-</math> <math display="block">-/-</math> <math display="block">-/-</math> <math display="block">-/-</math> <math display="block">-/-</math> <math display="block">-12/-29</math> <math display="block">-12/-29</math> <math display="block">40/88</math> <math display="block">67/120</math> <math display="block">-/11</math> <math display="block">-/11</math> <math display="block">-/-</math> <math display="block">-/-</math></td><td><math display="block">\begin{array}{c} C_4H_6 \\ \hline -/- \\ -22/-12 \\ -52/-43 \\ -52/-43 \\ 16/11 \\ -/- \\ -18/- \\ 27/- \\ -27/- \\ -/- \\ -/- \\ -50/-52 \\ -50/-52 \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ 214/107 \\ -100/-100 \\ -/- \\</math></td><td><math display="block">\begin{array}{c} \hline C_4 \\ \hline \\ -/- \\ -52/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ 26/- \\ 26/- \\ 26/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -39/- \\ -/- \\ -39/- \\ -/- \\ -39/- \\ -/- \\ -14 \\ -100/ \\ -99/- \\ -99/- \\ -99/- \\ -/- \\ -/14 \\ -/- \\ -/- \\ 50/- \\ -/ \\ -/- \\ 50/- \\ -/ \\ -/- \\ 50/- \\ -/ \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\</math></td><td>H2 -42 -42 -42 -42 </td><td><math display="block">\begin{array}{c} \hline C_4H_4 \\ \hline \\ </math></td></t<>	Lucts without           H4         C. $-/ -/ -37$ $-41$ $-37$ $-41$ $-7 -6/ 12/ -13$ $13$ $-/ 13$ $-/ -17$ $-18$ $-17$ $-18$ $-17$ $-18$ $-17$ $-18$ $-17$ $-18$ $-17$ $-18$ $-17$ $-18$ $-17$ $-18$ $-17$ $-18$ $-17$ $-18$ $-17$ $-18$ $-17$ $-16$ $-17$ $-18$ $-16$ $-17$ $-17$ $-16$ $-17$ $-16$ $-17$ $-16$ $-17$ $-17$ $-16$ $-17$ $-17$ $-17$ $-17$ $-17$ $-17$ $-17$ $-17$	t Nitrogen	$\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline \\ 18/- \\ 22/- \\ 22/- \\ 22/- \\ 22/- \\ 38/-18 \\ -20 \\ -20 \\ -20 \\ -20 \\ -20 \\ -30 \\ -15 \\ -15 \\ 50/-78 \\ -15 \\ 50/-78 \\ -48/-73 \\ 49/-24 \\ -24 \\ -24 \\ -27 \\ -24 \\ -27 \\ -24 \\ -27 \\ -24 \\ -27 \\ -2$	$\frac{C_{3}H_{4}}{-12/-}$ $-10/-$ $-20/-23$ $-20/-23$ $-20/-19$ $-23/-$ $-/-$ $-/-$ $-/-$ $-/-$ $-/-$ $-12/-29$ $-12/-29$ $40/88$ $67/120$ $-/11$ $-/11$ $-/-$	$\begin{array}{c} C_4H_6 \\ \hline -/- \\ -22/-12 \\ -52/-43 \\ -52/-43 \\ 16/11 \\ -/- \\ -18/- \\ 27/- \\ -27/- \\ -/- \\ -/- \\ -50/-52 \\ -50/-52 \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ 214/107 \\ -100/-100 \\ -/- \\$	$\begin{array}{c} \hline C_4 \\ \hline \\ -/- \\ -52/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ 26/- \\ 26/- \\ 26/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -39/- \\ -/- \\ -39/- \\ -/- \\ -39/- \\ -/- \\ -14 \\ -100/ \\ -99/- \\ -99/- \\ -99/- \\ -/- \\ -/14 \\ -/- \\ -/- \\ 50/- \\ -/ \\ -/- \\ 50/- \\ -/ \\ -/- \\ 50/- \\ -/ \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\$	H2 -42 -42 -42 -42 	$\begin{array}{c} \hline C_4H_4 \\ \hline \\ $
$\begin{array}{c} \text{no} \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 7 \\ 8 \\ 9 \\ 10 \\ 13 \\ 14 \\ 15 \\ 166 \\ 17 \\ 18 \\ 29 \\ 30 \\ 33 \\ 34 \\ 43 \\ 44 \\ 45 \\ 46 \\ 48 \\ 49 \\ 50 \\ 51 \\ 52 \\ 53 \\ 56 \\ 57 \\ 59 \\ \end{array}$	reactionsDMPyrrole → DMPyrrole(R1) + H*DMPyrrole → DMPyrrole(R2) + H*DMPyrrole → MPyrrole(R1) + CH3*DMPyrrole → MPyrrole(R2) + CH3*DMPyrrole + H* → DMPyrrole(R1) + H2DMPyrrole + CH3* → DMPyrrole(R1) + H2DMPyrrole + CH3* → DMPyrrole(R1) + CDDMPyrrole + H* → 2-MPyrrole + CH3*DMPyrrole + H* → 2-MPyrrole + CH3*DMPyrrole(R1) → C3H4 + C2H4CN*DMPyrrole(R1) → C3H4 + C2H4CN*DMPyrrole(R1) → C3H4 + CH2MPyrrole(R2) → C3H4 + CH2CN*MPyrrole(R2) → C3H4 + CH2CN*MPyrrole(R2) → C3H4 + CH2CN*DMPyrrole(R1) → 5-Picoline + H*DMPyrrole(R2) → 2-Picoline + H*DMPyrrole(R2) → 2-Picoline + H*MPyrrole(R2) → Pyridine + H*MPyrrole(R2) → Pyridine + H*MPyrrole(R2) + H* → 2-MPyrroleMPyrrole(R2) + H* → 2-MPyrroleAMPyrrole(R1) + H* → 4-MPyrroleMPyrrole(R2) + H* → 2-MPyrroleMPyrrole(R4) → Pyridine + H*MPyrrole(R4) + Pyrrole(R3) + CH4-AH5* + H* → C4H6C4H3* → C4H2 + H*C4H4 + H* → C4H3* + H2C2H6 + H* → C2H3* + H2C2H6 + H* → C2H3* + CH4C4H3* + CH3* → C2H5* + H*C4H6* → CH4* → C2H5* + H*C4H6* → CH3* → C2H5* + H*C4H6* → CH3* → C2H5* + H*C4H6* → CH4* → C4H6C4H5* → C4H6C4H5* → C4H6C4H6* → CH3* → C2H5* + H*C4H6* → CH3* → C2H5* + H*C4H6* → CH3* → C2H5* + H*C4H6	$\begin{array}{c} CF \\ \hline -/- \\ -10/- \\ -25/- \\ -25/- \\ -25/- \\ -10/- \\ -35/- \\ -10/- \\ -10/- \\ -10/- \\ -/ \\ -/- \\ -/- \\ -/ \\ -/- \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/ \\ -/$	B. Prod           I4         C21           -/-         -/-           -13         -14/           -19         -49/           -10         21/-           -13         -13/           -13         -13/           -13         -13/           -13         -13/           -14/         -/-           -/- <t< td=""><td>Lucts without           H4         C.           <math>-/ -/ -37</math> <math>-41</math> <math>-37</math> <math>-41</math> <math>-7 -6/ -137</math> <math>-41</math> <math>-12/ -13</math> <math>137</math> <math>-141</math> <math>-17</math> <math>-183</math> <math>-1-17</math> <math>-188</math> <math>-17</math> <math>-188</math> <math>-17</math> <math>-188</math> <math>-177</math> <math>-188</math> <math>-177</math> <math>-188</math> <math>-177</math> <math>-188</math> <math>-177</math> <math>-188</math> <math>-177</math> <math>-188</math> <math>-177</math> <math>-167</math> <math>-177</math> <math>-175</math> <math>-175</math> <math>-175</math> <math>-175</math> <math>-175</math> <math>-176</math> <math>-176</math></td><td>t Nitrogen</td><td><math display="block">\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline \\ 18/- \\ 22/- \\ 22/- \\ 22/- \\ 22/- \\ 22/- \\ 38/-18 \\ -20 \\ -20 \\ -20 \\ -20 \\ -20 \\ -30 \\ -15 \\ -15 \\ 50/-78 \\ 48/-73 \\ 49/-24 \\ -24 \\ -24 \\ -27 \\ -24 \\ -27 \\ -24 \\ -27 \\</math></td><td><math display="block">\frac{C_{3}H_{4}}{-12/-}</math> <math display="block">-10/-</math> <math display="block">-20/-23</math> <math display="block">-20/-23</math> <math display="block">-20/-19</math> <math display="block">-23/-</math> <math display="block">-/-</math> <math display="block">-/-</math> <math display="block">-/-</math> <math display="block">-/-</math> <math display="block">-/-</math> <math display="block">-12/-29</math> <math display="block">-12/-29</math> <math display="block">40/88</math> <math display="block">67/120</math> <math display="block">-/11</math> <math display="block">-/11</math> <math display="block">-/-</math> <math display="block">-/-</math></td><td><math display="block">\begin{array}{c} C_4H_6 \\ \hline -/- \\ -22/-12 \\ -52/-43 \\ -52/-43 \\ 16/11 \\ -/- \\ -18/- \\ 27/- \\ -27/- \\ -/- \\ -50/-52 \\ -50/-52 \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ 214/107 \\ -100/-100 \\ -/- \\</math></td><td><math display="block">\begin{array}{c} \hline C_4 \\ \hline \\ -/- \\ -52/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ 26/- \\ 26/- \\ 26/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -39/- \\ -/- \\ -39/- \\ -/- \\ -14 \\ -100/ \\ -99/- \\ -99/- \\ -99/- \\ -/- </math></td><td>H2 -42 -42 -42 -42 -42 </td><td><math display="block">\begin{array}{c} \hline C_4H_4 \\ \hline \\ </math></td></t<>	Lucts without           H4         C. $-/ -/ -37$ $-41$ $-37$ $-41$ $-7 -6/ -137$ $-41$ $-12/ -13$ $137$ $-141$ $-17$ $-183$ $-1-17$ $-188$ $-17$ $-188$ $-17$ $-188$ $-177$ $-188$ $-177$ $-188$ $-177$ $-188$ $-177$ $-188$ $-177$ $-188$ $-177$ $-167$ $-177$ $-175$ $-175$ $-175$ $-175$ $-175$ $-176$ $-176$ $-176$ $-176$ $-176$ $-176$ $-176$ $-176$ $-176$ $-176$ $-176$ $-176$ $-176$ $-176$ $-176$ $-176$ $-176$ $-176$	t Nitrogen	$\begin{array}{c} C_2H_2 \\ \hline 15/- \\ 27/-11 \\ 38/-36 \\ 38/36 \\ \hline \\ 18/- \\ 22/- \\ 22/- \\ 22/- \\ 22/- \\ 22/- \\ 38/-18 \\ -20 \\ -20 \\ -20 \\ -20 \\ -20 \\ -30 \\ -15 \\ -15 \\ 50/-78 \\ 48/-73 \\ 49/-24 \\ -24 \\ -24 \\ -27 \\ -24 \\ -27 \\ -24 \\ -27 \\$	$\frac{C_{3}H_{4}}{-12/-}$ $-10/-$ $-20/-23$ $-20/-23$ $-20/-19$ $-23/-$ $-/-$ $-/-$ $-/-$ $-/-$ $-/-$ $-12/-29$ $-12/-29$ $40/88$ $67/120$ $-/11$ $-/11$ $-/-$	$\begin{array}{c} C_4H_6 \\ \hline -/- \\ -22/-12 \\ -52/-43 \\ -52/-43 \\ 16/11 \\ -/- \\ -18/- \\ 27/- \\ -27/- \\ -/- \\ -50/-52 \\ -50/-52 \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ -/- \\ 214/107 \\ -100/-100 \\ -/- \\$	$\begin{array}{c} \hline C_4 \\ \hline \\ -/- \\ -52/- \\ -52/- \\ -52/- \\ 16/10 \\ -/- \\ 26/- \\ 26/- \\ 26/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -50/- \\ -/- \\ -39/- \\ -/- \\ -39/- \\ -/- \\ -14 \\ -100/ \\ -99/- \\ -99/- \\ -99/- \\ -/- $	H2 -42 -42 -42 -42 -42 	$\begin{array}{c} \hline C_4H_4 \\ \hline \\ $

-/-<sup>a</sup> 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

 $C_2H_3^{\bullet} \rightarrow C_2H_2 + H^{\bullet}$ 

60

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.

Acknowledgment. This work was supported by a grant from the BSF, US-Israel Binational Science Foundation under Grant agreement 98-00076. We thank Prof. Hai Wang our American co-investigator for many fruitful discussions.

#### **References and Notes**

(1) Lifshitz, A.; Tamburu, C.; Suslensky, A. J. Phys. Chem. 1989, 93, 5802.

(2) Mackie, J. C.; Colket, M. B., III.; Nelson, P. F; Esler, M. Int. J. Chem. Kinet. 1991, 23, 733

(3) Martoprawiro, M.; Backsay, G. B; Mackie, J. C. J. Phys. Chem. A 1999, 103, 3934.

(4) Dubnikova, F; Lifshitz, A. J. Phys. Chem. A 1998, 102, 10880.

(5) Zhai, L.; Zhou, X and Liu, R. J. Phys. Chem. A 1999, 103, 3917.
(6) Doughty, A.; Mackie, J. C; Backsay, G. B. Chem. Phys. Lett. 1994,

221, 267.
(7) Dubnikova, F; Lifshitz, A. J. Phys. Chem. A 2000, 104, 530.

(7) Dubinkova, 1, Ensinez, A. J. Phys. Chem. A 2000, 104, 530.
(8) Lifshitz, A.; Shweky, I; Tamburu, C. J. Phys. Chem. 1993, 97,

(d) Ensinez, A., Shweky, I, Tanburd, C. J. Thys. Chem. 1995, 4442.

(9) Laskin, A; Lifshitz, A. J. Phys. Chem. A 1997, 101, 7787.

(10) Zhou, X; Liu, R. THEOCHEM 1999, 461, 567.

(11) Smith, B. J; Liu, R. THEOCHEM 1999, 491, 211.

(12) Dubnikova, F; Lifshitz, A. J. Phys. Chem. A 2001, 105, 3605-3614.

(13) Tsang, W.; Lifshitz, A. Int. J. Chem. Kinet. 1998, 30, 621.

(14) Lifshitz, A.; Bidani, M; Bidani, S. J. Phys. Chem. 1986, 90, 3422.

(15) Lifshitz, A.; Bidani, M; Bidani, S. J. Phys. Chem. 1986, 90, 5373.

(16) Lifshitz, A; Wohlfeiler, D. J. Phys. Chem. 1992, 96, 4505.

(17) Lifshitz, A; Wohlfeiler, D. J. Phys. Chem. 1992, 96, 7367.

(18) Westly, F.; Herron, J. T.; Cvetanovic, R. J.; Hampson, R. F.; Mallard, W. G. *NIST-Chemical Kinetics Standard Reference database 17*,

Ver. 5.0; National Institute of Standards and Technology: Washington, DC. (19) Pedley, J. B.; Taylor, R. D; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986.

(20) Burcat, A.; McBride, B; Rabinowitz, M. *Ideal Gas Thermodynamic Data for Compounds Used in Combustion* T. A. E. 657 report; Technion–Israel Institute of Technology: Haifa, Israel, 2002.

(21) Warnatz, J. Rate coefficients in the C/H/O system. In *Combustion Chemistry*; Gardiner, W. C., Jr., Ed.; Springer-Verlag: New York, 1984.

(22) Stein, S. E.; Rukkers, J. M; Brown, R. L. *NIST-Standard Reference database 25*; National Institute of Standards and Technology: Washington, DC.

(23) Muller, C.; Warth, V.; Jacquemard, E.; Scacchi, G.; Come, G. M. A FORTRAN computer code package for the evaluation of thermochemical data of molecules, free radicals and reactions in the gas phase and A. S. T. M. CHETAH safety criteria. ENSIC-INPL, University of Nancy I: Nancy, France, 1996.

(24) Tsang, W.; Hampson, R. F. J. Phys. Chem. Ref. Data 1986, 15, 1087.

(25) Tsang, W. Combust. Flame 1989, 78, 71.

(26) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Esser, C.; Frank, P.; Just, Th.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. J. *Phys. Chem. Ref. Data* **1992**, *21*, 411–429.

(27) Lifshitz, A.; Tamburu, C.; Carroll, H. F. Int. J. Chem. Kinet. 1997, 29, 839-849.

(28) Lifshitz, A.; Tamburu, C. Int. J. Chem. Kinet. 1998, 30, 341–347.

(29) Lifshitz, A.; Tamburu, C; Shashua, R. J. Phys. Chem. A 1997, 101, 1018.