compatible microcomputer. Thus, this procedure is applicable to real time, on-line kinetic analysis and model testing.

Precision in the rate constants of the two more slowly decomposing anion radicals was excellent. However, a visible trend seen in Tables III and IV is the deterioration of precision in k at higher rates. While work is being done to fully explain the cause of such behavior, we feel that it is mainly a limitation of electrode size and data acquisition rate of 1 point/ms. Analysis of data for faster reactions is more heavily influenced by instrumental errors in the measured charge. Also, deviation from the model due to the time dependence of charging of the electrode double layer (Q_{dl}) is most pronounced in the first few milliseconds after the potential step. This also contributes to degraded precision for larger rate constants where most of the kinetic information is contained at short times.[2] This limitation may possibly be removed by using ultramicroelectrodes, decreasing the time window into the submillisecond range and increasing the rate at which data are collected. Such an approach may also require incorporation of the time dependence of Q_{dl} in the model.

Orthogonalization necessitates *deriving* an orthogonal form of the model. After the values of regression parameters are obtained by use of such a model, deconvolution to recoup the original set of parameters is required. Fortunately, the nature of Gram–Schmidt orthogonalization should eventually enable fully automated transitions between the original basis set and the orthogonal one. It is not necessary or practical to use an orthogonalized model for every problem to be solved by nonlinear regression analysis. However, our results demonstrate the usefullness of orthogonalization when serious correlation between parameters creates problems in convergence of nonlinear regression analyses. Since the transformation is made on the model, the method is compatible with currently used general programs for nonlinear regression.

Isomerization and Decomposition of Pyrrole at Elevated Temperatures. Studies with a Single-Pulse Shock Tube

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The thermal decomposition of pyrrole was studied behind reflected shocks in a pressurized driver single-pulse shock tube over the temperature range 1050–1450 K and overall densities of $\sim$3 × 10^{-5} mol/cm^3. Under these conditions the nitrogen-containing products found in the postshock mixtures were *cis*-CH$_3$CH=CHCN, HCN, CH$_2$=CH—CH$_2$CN, *trans*-CH$_3$CH=CHCN, CH$_3$CN, CH$_2$=CHCN, C$_2$H$_5$CN, CH≡C—CN, and small quantities of C$_6$H$_5$CN, C$_6$H$_5$CH$_2$CN, CH$_2$=C=CHCN and CH$_3$C≡C—CN which began to appear at the high end of the temperature range. Products without nitrogen were CH$_3$C≡CH, CH≡CH, CH$_2$=C=CH$_2$, CH$_4$, C$_2$H$_4$, and small quantities of C$_4$H$_6$, C$_4$H$_4$, C$_4$H$_2$, C$_6$H$_6$, C$_6$H$_5$C≡CH, and C$_6$H$_5$CH$_3$ which appeared only at high temperatures. The main reaction of pyrrole under these conditions is a simultaneous unimolecular bond cleavage in the 1–5 (1–2)-position and a hydrogen atom transfer, followed by electronic rearrangement and (1) isomerization to *cis*-crotonitrile, (2) dissociation to HCN + C$_3$H$_4$ (mainly propyne) and (3) isomerization to allyl cyanide, with a branching ratio of approximately 3.5:1.5:1. The overall process proceeds with a rate constant of $k = 10^{14.83} \exp(-75 × 10^3/RT)$ s^{-1}, where R is expressed in units of cal/(K·mol). The second major reaction of pyrrole is a dissociation to acetylene and CH$_2$=C=NH. Decomposition and isomerization of the initiation products as well as additional free-radical reactions lead to the formation of a plethora of reaction products. Arrhenius rate parameters for their formation are reported and a general pyrolysis scheme is suggested.

Introduction

We have recently published a series of studies on the thermal reactions of five-membered ring ethers: furan,[1] tetrahydrofuran,[2] and 2,3- and 2,5-dihydrofuran,[3,4] discussing their pyrolysis mechanism and reporting Arrhenius parameters for the production rates of the pyrolysis products. The pyrolysis of pyrrolidine, the nitrogen analogue of tetrahydrofuran, was also recently investigated behind reflected shocks,[5] stressing the differences and similarities between the nitrogen- and oxygen-containing heterocyclics.

Pyrrole is the nitrogen analogue of furan. Its skeleton appears in a large number of naturally occurring structures as well as in

the major constituents of fuel nitrogen.[6,7] As far as we are aware its thermal reactions at elevated temperatures have never been studied in the past. In addition to the interest in the basic chemical kinetics of these compounds, they are of great relevance to combustion technology. Their thermal behavior both under pyrolytic and oxidative environments simulate the reactions that occur during the combustion of a large variety of nitrogen-containing fuel molecules.

This article presents a continuous effort in elucidating the kinetics and mechanism of the thermal reactions of oxygen- and nitrogen-containing heterocyclics. It discusses in detail the thermal reactions of pyrrole with a special emphasis on the differences and similarities with its oxygen analogue, furan.

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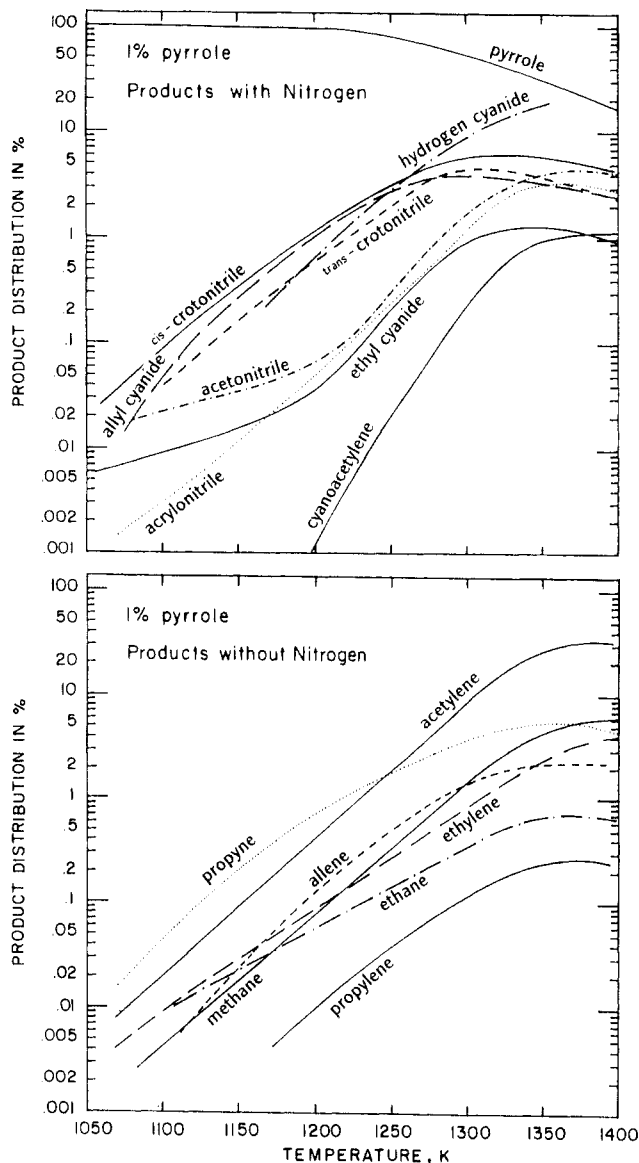
Experimental Section

Apparatus. The reactions of pyrrole were studied behind reflected shocks in a pressurized driver single-pulse shock tube made of 52 mm i.d. electropolished stainless steel tubing. The driven section was 4 m long and the driver had a variable length up to a maximum of 2.7 m and could be varied in small steps in order to tune for the best cooling conditions. A 36-L dump tank was connected to the driven section at 45° angle toward the driver, near the diaphragm holder, to prevent reflection of transmitted waves and to reduce the final pressure in the tube to facilitate the extraction of gas samples. The driven section was separated from the driver by Mylar polyester film of various thickness depending upon the desired shock strength.

Prior to the experiment the tube was pumped down to approximately 2×10^{-5} Torr. After firing the shock, gas samples were collected from the tube and were analyzed by various methods as will be later described.

Reflected shock parameters were calculated from the measured incident shock velocities using the three conservation equations and the ideal gas equation of state. The incident shock velocities were measured with two miniature, high-frequency pressure transducers (Vibrometer Model 6QP500) placed 300 mm apart near the end plate of the driven section. The signals generated by the shock wave passing over the transducers were fed through a piezo amplifier to a Nicolet Model 3091 digital oscilloscope. Time intervals between the two signals shown on the oscilloscope were obtained digitally with an accuracy of 2 μs corresponding to 10–15 K depending upon the shock temperature. A third transducer (P.C.B. Model 113A26) placed at the center of the end plate provided measurements of the reaction dwell times (approximately 2 ms) with an accuracy of ~5%. Cooling rates were approximately 5×10^5 K/s.

A more detailed description of the tube and its mode of operation have been described in previous publications.[8]

Materials and Analysis. Reaction mixtures containing 1% pyrrole in argon were prepared manometrically and stored at 1 atm in 12-L glass bulbs. Both the bulbs and the vacuum line were pumped down to better than 10^{-5} Torr before preparation of the mixtures.

Pyrrole, listed as 99% pure, was obtained from Aldrich Chemical Co. None of the reaction products were found in the original material. Argon was Matheson ultra-high-purity grade, listed as 99.9995%, and helium was Matheson pure grade listed as 99.999%. All the materials were used without further purification.

Gas analyses were performed in the following manner: shocked samples were injected into the gas chromatograph (HP Model 5890) and were then equally divided between 2-m Porapak N and Tenax columns. The Porapak N column, connected to a FID, separated and quantitatively determined the reaction products without bound nitrogen. The Tenax column, connected to a NPD, separated and quantitatively determined all the nitrogen-containing species. The initial columns' temperature was 35 °C. It was gradually elevated to 170 °C in an analysis which lasted about 80 min.

In order to evaluate the concentrations of the reaction products from their GC peak areas the following measurements were made. First, the sensitivities of all the species were determined from standard mixtures relative to one major species in each column: hydrogen cyanide in Tenax and propyne in Porapak N. Then the ratio of the hydroen cyanide peak area to that of propyne in a mixture containing a 1:1 ratio of these two compounds was determined. With this ratio and the relative sensitivities, the data in the two chromatograms could be combined and the concentration of each product in shocked samples could be determined.

Typical chromatograms of a shocked mixture of 1% pyrrole in argon heated to 1275 K are shown in Figure 1.

The identification of the reaction products was based on their retention times in the gas chromatograph. To assist in the gas chromatographic identification, chromatograms were run also with

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Figure 1. Gas chromatograms of a postshock mixture of 1% pyrrole in argon heated to 1275 K, taken on a 2-m Tenax column using NPD and a 2-m Porapak N column using FID. (The numbers on the peaks are relative attenuation factors.)

a HP Model 5970 mass selective detector. Each mass spectrum at the peak height was compared with standard spectra[9] and the peak could be identified.

Identification of crotonitrile as cis isomer was done by NMR studies applying the double resonance technique.

GC peak areas were integrated with a Spectra Physics Model SP4200 dual channel computing integrator and were transferred to a C.D.C. CYBER 180/855 main frame computer for data reduction and graphical presentation.

Results

Product Distribution. In order to determine the distribution of reaction products in pyrrole pyrolysis and to determine the production rates of the various products, some 40 tests were performed with mixtures containing 1% pyrrole in argon, covering the temperature range 1050–1450 K. Figure 2 shows the distribution of products with and without bound nitrogen as obtained in postshock samples. The percent of a given product out of the total shown on the figures is its mole percent $(100C_i/\sum C_i)$ in the mixture irrespective of the number of its carbon atoms. (Molecular hydrogen is not included.) As can be seen (Figure 2), at the low-temperature range the isomerization products are the products of the highest concentration. The major product is *cis*-crotonitrile. The trans isomer appears at low concentration but approaches the cis isomer as the temperature increases. Allyl cyanide, a second isomer of pyrrole, is also a major product. Another pair of products which comes from the same transition structure as the isomerization products is propyne + hydrogen cyanide. At low temperatures propyne is the largest among the decomposition products without bound nitrogen. At higher temperatures the isomerization products as well as propyne take part in subsequent reactions with the formation of a large number of additional products.

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Figure 2. Distribution of reaction products in postshock mixtures of 1% pyrrole in argon shown over the temperature range 1050–1400 K. The major products are the isomerization products of pyrrole, hydrogen cyanide, and propyne.
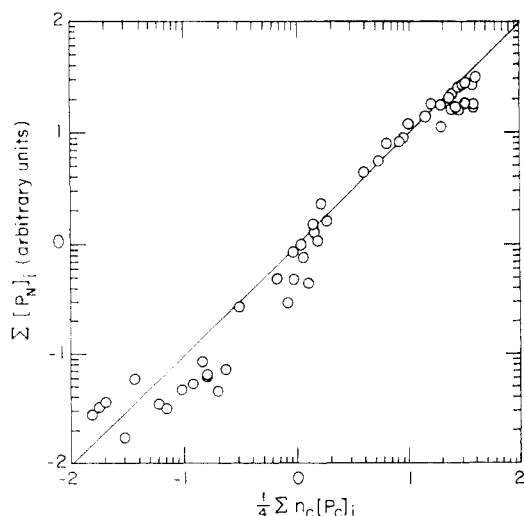

Figure 3. Plot of $\sum [P_{N_i}]$ vs $^1/_4\sum(n_{C_i}[P_{C_i}])$ which shows the nitrogen–carbon mass balance among the decomposition products (see text).

Nitrogen–Carbon Balance. The balance of nitrogen vs carbon in the decomposition products is shown in Figure 3. The con-
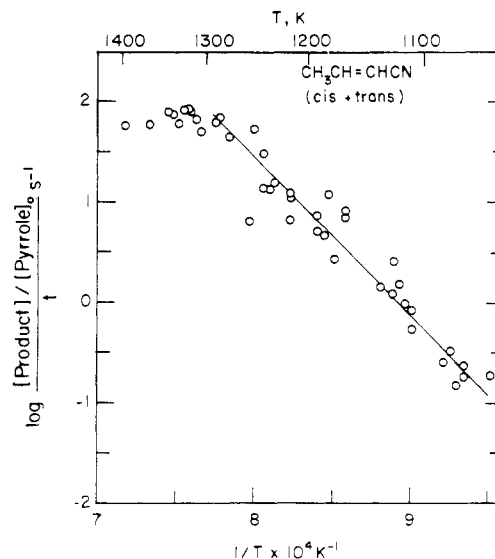
Figure 4. Production of crotonitrile (cis + trans). The slope of the line gives the Arrhenius activation energy for the isomerization reaction: pyrrole → crotonitrile. $E = 72$ kcal/mol.
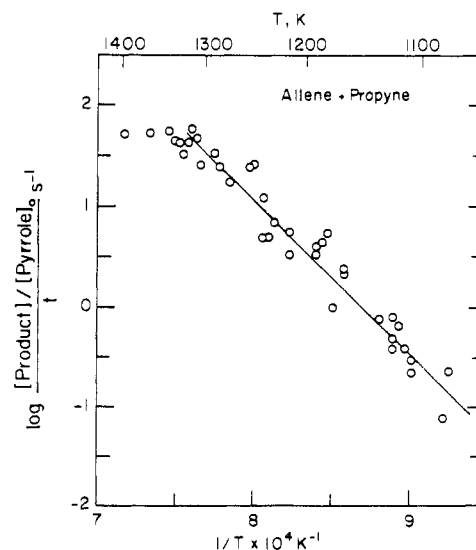
Figure 5. Production of C_3H_4 (allene + propyne). The line corresponds to the first-order rate constant of the major reaction: pyrrole → HCN + C_3H_4.

centrations of all the nitrogen-containing species (not including the crotonitriles and ally cyanide) $\sum [P_{N_i}]$ are plotted against the sum of the concentrations of all the species $^1/_4\sum(n_{C_i}[P_{C_i}])$, where $[P_{N_i}]$ is the concentration of a nitrogen-containing species, n_{C_i} is the number of carbon atoms in a species i, and $[P_{C_i}]$ is the concentration of a species i. The diagonal in the figure represents a perfect mass balance. The species that carries most of the nitrogen in the system is hydrogen cyanide. As can be seen, a nitrogen–carbon balance is maintained with some tendency toward a slight loss of nitrogen relative to carbon. This will be discussed later.

Arrhenius Rate Parameters. In Figures 4–8, the production rates of several of the reaction products defined as:

$$\text{rate}(\text{pr}_i) = [\text{pr}_i]_t/t$$

and divided by the initial pyrrole concentration are plotted on a logarithmic scale against reciprocal temperature in units of s^{-1}. The cis and trans isomers of crotonitrile as well as the two structural isomers of C_3H_4, propyne and allene, are plotted on the same figure to produce a single rate constant. It is believed that in each pair one isomer is produced by the isomerization of the other, as will be discussed later.
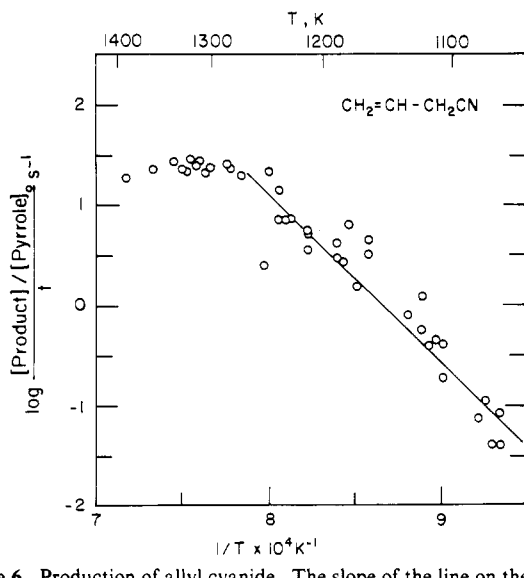
Figure 6. Production of allyl cyanide. The slope of the line on the figure corresponds to an activation energy of 77 kcal/mol for the isomerization reaction: pyrrole → allyl cyanide.
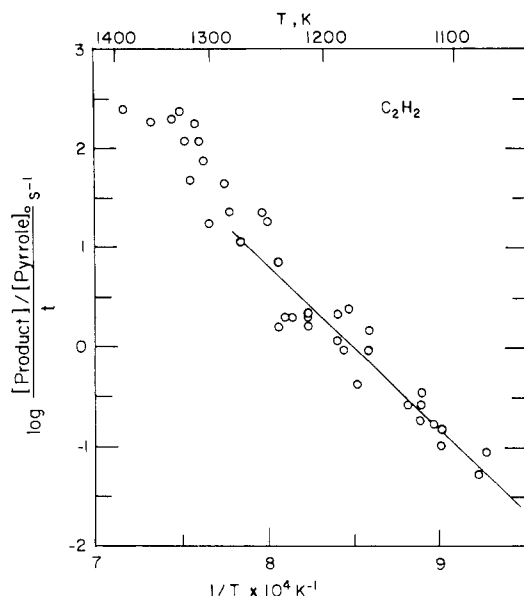
Figure 7. Acetylene production. Acetylene is produced mainly by a direct dissociation from the pyrrole ring with small contribution from the decomposition of propyne. Its Arrhenius parameters do not correspond to a simple unimolecular reaction.

Figure 8. Producton of cyanoacetylene. Cyanoacetylene is one of the minor products of the pyrolysis. The slope of the line on the plot corresponds to an exponential temperature dependence of 158 kcal/mol.
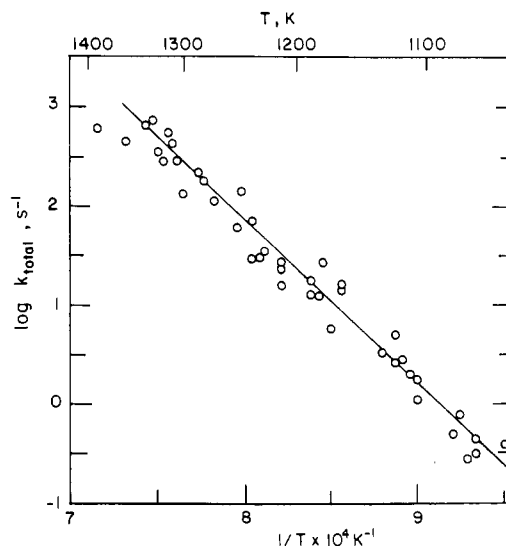
Figure 9. Arrhenius plot for the overall decomposition of pyrrole. k_{total} = $10^{15.90}$ exp($-80 \times 10^3/RT$) s^{-1}.

TABLE I: Preexponential Factors (A) and Arrhenius Temperature Dependences (E) for the First-Order Rate Constants of Formation of Various Reaction Products

compound	log A, s^{-1}	E, kcal/mol	T, K
pyrrole[a] (initiation)	14.83	75	1050–1250
pyrrole[b] (total)	15.90	80	1050–1250
CH$_3$CN=CHCN (cis + trans)	14.02	72	1050–1250
C$_3$H$_4$ (propyne + allene)	13.80	73	1075–1250
CH$_2$=CH$_2$CHCN	14.60	77	1050–1250
C$_2$H$_2$	14.28	77	1080–1280
HCN	15.80	84	1175–1335
CH$_2$=CHCN	12.28	67	1140–1340
CH≡C—CN	26.58	158	1200–1340

[a] First-order rate constant for the major initiation process of pyrrole. [b] First-order rate constant for the overall decomposition of pyrrole.

At low extents of reaction the points of these plots scatter along a straight line and can be considered as true first-order rate constants. At high conversions (high temperatures) this presentation is no longer meaningful. Some of the plots show a bend owing to the depletion of the reactant and subsequent reactions of the products.

Values of E obtained from the slopes of the lines and their corresponding preexponential factors are summarized in Table I, in units of kcal/mol and s^{-1}, respectively.

It should be stressed that although the values in Table I correspond to first order rate parameters they do not always represent elementary unimolecular reactions. They are useful as a basis for computer modeling of the decomposition scheme.

Figure 9 shows the overall decomposition rate constants of pyrrole, k_{total}, calculated from its disappearance rate:

$$k_{total} = -(1/t) \ln \{1 - [\text{pyrrole}]_t / [\text{pyrrole}]_0\}$$

The Arrhenius parameters obtained for the overall disappearance of pyrrole (which do not correspond to a true unimolecular reaction) are k_{total} = $10^{15.90}$ exp($-80 \times 10^3/RT$) s^{-1}.

Discussion

Isomerization Reactions. As has been demonstrated, two isomerization reactions and one fragmentation constitute the major reactions of pyrrole. They yield (1) *cis*-crotonitrile, (2) propyne + HCN, and (3) allyl cyanide, with a branching ratio of approximately 3.5:1.5:1. These three reaction channels come from
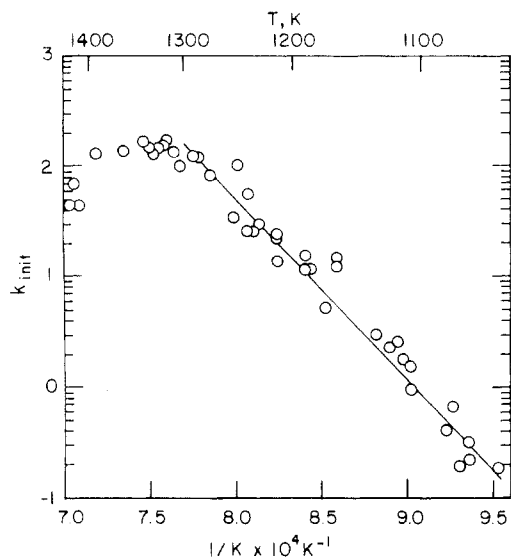
Figure 10. Arrhenius plot for the major initiation process. It corresponds to the production rates of crotonitrile (cis and trans), C_3H_4 (propyne + allene), and allyl cyanide. The rate constant obtained for this process is $k_1 = 10^{14.83} \exp(-75 \times 10^3/RT)$ s^{-1}.

a single transition structure which involves a simultaneous unimolecular C–N bond cleavage in the 1–5 (1–2)-position and a hydrogen atom transfer followed electronic rearrangement:

$$(cis\text{-Crotonitrile}) \quad (1)$$

$$CH_2^-\!-CH\!=\!CH^{\cdot} + HCN \rightarrow CH_3C\!\equiv\!CH + HCN \quad (2)$$
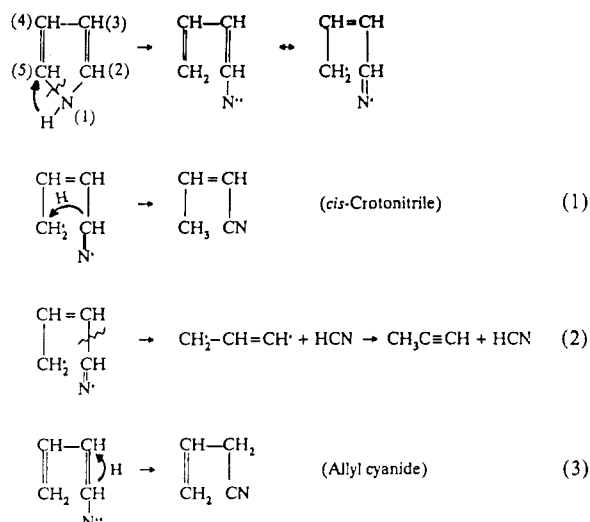
$$(Allyl\ cyanide) \quad (3)$$

In order to obtain the Arrhenius rate parameters for the major initiation step, the sum of the rates of these three processes (which includes the rate of formation of *cis*- and *trans*-crotonitrile, propyne + allene, and allyl cyanide) is plotted on a logarithm scale vs reciprocal temperature in Figure 10. The line on the figure covers a temperature range over which the sum of the concentrations of these products is considerably higher than the sum of all the others so that secondary reactions are negligible. The straight line on the figure represents an Arrhenius curve which corresponds to the rate of the major initiation. The rate constant obtained for this process is $k_{init.} = 10^{14.83} \exp (-75 \times 10^3/RT)$ s^{-1}.

The activation energy of the initial reaction is considerably higher than the endothermicity of the individual steps.[10,11]

$$\rightarrow cis\text{-}CH_3CH\!=\!\!=\!CHCN \quad \Delta H_1^\circ = 6.2\ kcal/mol$$

$$\rightarrow CH_3C\!\equiv\!CCH + HCN \quad \Delta H_2^\circ = 49.6\ kcal/mol$$

$$\rightarrow CH_2\!=\!\!=\!CHCH_2CN \quad \Delta H_3^\circ = 9.3\ kcal/mol$$
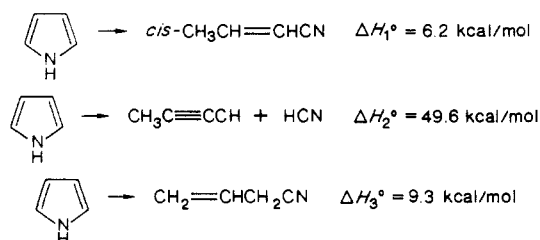
The rates of the three individual channels are shown in Figures 4–6 and their Arrhenius parameters are listed in Table I. We have made some log–log plots of pairs of initiation products in order to assess whether the observed branching ratio of the three individual processes are due to differences in their activation energies or preexponential factors. Although such plots eliminate the temperature errors (which are normally the main source of error in shock-tube kinetics), the results were inconclusive because of the scatter in the experimental data caused by the gas chromatographic analysis. The analysis of nitrogen-containing species with NPD is extremely sensitive but not always reproducible. The cleavage of the carbon–nitrogen bond and the migration of a hydrogen atom from the nitrogen to an adjacent carbon constitutes the reaction barrier.

The geometry of the transition structure dictates that only the cis isomer of crotonitrile can be formed directly from pyrrole (reaction 1). Indeed, at low temperatures only the cis isomer is found. As the temperature increases, the latter isomerizes to the trans isomer until cis–trans equilibrium is attained, the cis being more stable that the trans.[12] This can readily be seen in Figure 2.

It should be pointed out that such isomerizations in furan, the oxygen analogue of pyrrole, were not observed.[1] Products such as allenecarboxaldehyde ($CH_2\!=\!C\!=\!CH\!-\!CHO$) and propyne-carboxaldehyde ($CH_3C\!\equiv\!C\!-\!CHO$) which are isomers of furan and could have been formed during its pyrolysis were not found in the postshock mixtures.

The main thermal reaction in furan is a dissociation to propyne and carbon monoxide.[1] The equivalent process is pyrrole would be the dissociation to propyne and hydrogen cyanide. Whereas the latter does take place in pyrrole it is only one of three major channels and not the main one.

An important question that should be asked is whether the channel $C_4H_5N \rightarrow CH_3C\!\equiv\!CH + HCN$ takes place by the direct decomposition of pyrrole as has already been suggested, or else by elimination of HCN from its major isomerization product, crotonitrile. The elimination from the cis isomer may take place by attaching one of the hydrogen atoms of the methyl group to the CN to form HCN, and from the trans isomer by removing H and CN from the two carbon atoms of the C=C double bond. Elimination from the cis isomer leaves the radical $CH_2{}^{\bullet}\!-\!CH\!=\!CH^{\bullet}$ which may then stabilize to either propyne or allene. Elimination of HCN from the trans isomer produces propyne directly.

Elimination of HCN from organic nitriles is a known process.[13] Such a process in acrylonitrile, an unsaturated organic nitrile, has recently been studied in this laboratory.[14] Production of HCN and $CH\!\equiv\!CH$ is indeed the main reaction of acrylonitrile but production of molecular hydrogen and $CH\!\equiv\!C\!-\!CN$ from this molecule is also a major channel.[14] Were the reaction $CH_3C\-H\!=\!CHCN \rightarrow C_3H_4 + HCN$ an important reaction under our experimental conditions then one could expect also cyanoallene or cyanopropyne to be present in the postshock mixtures. These compounds were not formed, appearing only at very high temperatures and in trace quantities.

It is still possible that the decomposition of crotonitrile to HCN and C_3H_4 does occur at high temperatures but it cannot constitute the major channel for the production of the latter. Elimination of HCN from unsaturated nitriles takes place also by a free-radical mechanism. At high temperatures where decomposition of allyl cyanide and crotonitrile may contribute to the production of HCN and C_3H_4 they can be produced also by a free-radical mechanism. We believe however that, at low temperatures where the only source for HCN and C_3H_4 is pyrrole, they are produced by the

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(11) Pedly, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986.

(12) Butler, N. J.; McAlpine, R. D. *Can. J. Chem.* **1963**, *41*, 2487.

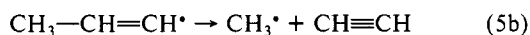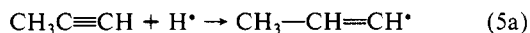(13) Dastoor, P. N.; Emovon, E. U. *Can. J. Chem.* **1973**, *51*, 366.

(14) Lifshitz, A.; Bidani, M.; Suslensky, A.; Tamburu, C. *J. Phys. Chem.* **1989**, *93*, 1369.

same transition structure which leads to the production of the isomerization products, namely, by a direct unimolecular reaction.

Acetylene Production. As can readily be seen in Figure 2, acetylene is the second major product among the products without bound nitrogen. At high temperatures it is the product of the highest concentration. A question that should be answered in this context is whether acetylene is a primary product which is produced directly from the pyrrole ring

$$\text{pyrrole} \longrightarrow CH\equiv CH + CH^{\bullet}{=}CH{-}NH^{\bullet} \qquad (4)$$
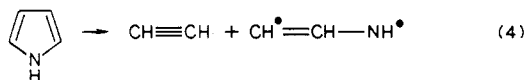
or whether it is a product of decomposition of propyne

$$CH_3C\equiv CH + H^{\bullet} \rightarrow CH_3{-}CH{=}CH^{\bullet} \qquad (5a)$$

$$CH_3{-}CH{=}CH^{\bullet} \rightarrow CH_3^{\bullet} + CH\equiv CH \qquad (5b)$$

or allyl cyanide

$$CH_2{=}CH{-}CH_2CN \rightarrow CH_2{=}CH^{\bullet} + CH_2CN^{\bullet} \qquad (6a)$$

$$CH_2{=}CH^{\bullet} \rightarrow CH\equiv CH + H^{\bullet} \qquad (6b)$$

which are major isomerization and decomposition products of pyrrole.

A similar question was raised when the pyrolysis of furan,[1] the oxygen analogue of pyrrole, was studied: was acetylene formed directly from the furan ring or alternatively via decomposition of propyne which was also found to be the major product of the pyrolysis.[1] By considerations of production rates and their temperature dependence it could easily be concluded that at low temperatures the only channel for acetylene production in furan could be elimination from the ring. The possibility of propyne being the precursor of acetylene was ruled out.

This question in pyrrole should be examined using the same considerations. The production rate of acetylene from propyne can be described by a first-order rate constant: $k = 10^{17.45} \exp(-96 \times 10^3/RT)$ s^{-1} (R is expressed in units of cal/(K·mol).[15] The production of acetylene from pyrrole shown in Figure 7 has at low temperatures a first-order rate constant of $k_4 = 10^{14.28} \exp(-77 \times 10^3/RT)$ s^{-1}. The production of propyne from pyrrole shown in Figure 5 proceeds with a rate constant of $k_2 = 10^{13.80} \exp(-73 \times 10^3/RT)$ s^{-1}. The concentration ratio of acetylene to propyne in the postshock mixtures is therefore given by the relation: $[\text{acetylene}]/[\text{propyne}] = 10^{1.04} \exp(-7 \times 10^3/RT)$ s^{-1}. This relation around 1150 K yields approximately 0.4 whereas a ratio of only 3.4×10^{-4} can be expected from the pyrolysis of propyne. This rules out the possibility that pyrolysis of propyne is the main route for acetylene production.

Moreover, were reaction 5b the major source for acetylene, then it should have led (over the temperature range in question) to the relation

$$[CH\equiv CH] \approx [CH_4] + 2[C_2H_6]$$

which has been demonstrated in the past to hold in propyne pyrolysis over a wide temperature range.[15] This relation is not valid in the present study.

The same considerations apply to the question of whether acetylene is a product of the pyrolysis of allyl cyanide (reaction 6). We do not have the rate parameters for the production of acetylene from allyl cyanide, but the ratio ([acetylene]/[propylene])$_{2\,ms}$ in the pyrolysis of propylene can serve as a good indicator.[16] The ratio that can be expected in propylene pyrolysis is by orders of magnitude smaller than the ratio [acetylene]/[allyl cyanide] observed in the pyrolysis of pyrrole.

One may therefore conclude that the main source for acetylene production is the decomposition of pyrrole

$$\text{pyrrole} \longrightarrow CH\equiv CH + CH^{\bullet}{=}CH{-}NH^{\bullet} \qquad (4)$$
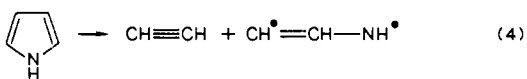
and not the decomposition of one of its pyrolysis or isomerization products.

At high temperatures these additional sources for acetylene production become significant. The temperature dependence of its rate increases with temperature as the result of this behavior (Figure 7) but at the low-temperature range (~ 1080–1280 K) the rate constant of $k_4 = 10^{14.28} \exp(-77 \times 10^3/RT)$ s^{-1} corresponds to the unimolecular ring cleavage represented by reaction 4.

The transition structure which leads to the formation of acetylene from propyne is entirely different from the one which leads to the formation of propyne and hydrogen cyanide. For the production of the latter a hydrogen atom must migrate from the nitrogen to an adjacent carbon simultaneously with the cleavage of the C–N bond. This does not occur when acetylene is produced.

Secondary Reaction Products. a. Products without Nitrogen. As can be seen in Figure 2, allene has the highest concentration among the secondary reaction products without bound nitrogen. It is produced by the isomerization of propyne.[17] At low temperatures the ratio [allene]/[propyne] is very low. As the temperature increases the rate of propyne $\rightarrow$ allene isomerization increases until equilibrium is attained at a ratio of approximately 1:3.

Both propyne and allene produce in their pyrolysis a spectrum of products as has been shown in previous investigations. Methane is a major product in the pyrolysis of propyne whereas allene is a precursor to ethylene.[15] Except for a study on the cis–trans isomerization of crotonitrile[12] we are unaware of recent studies on the thermal reactions of crotonitrile or allyl cyanide at high temperatures so that data on their decomposition is not known. The production of methyl and cyanovinyl radicals in the decomposition of crotonitrile

$$CH_3CH{=}CHCN \rightarrow CH_3^{\bullet} + CH^{\bullet}{=}CHCN \qquad (1b)$$
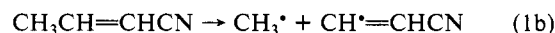
and the production of vinyl and cyanomethyl radicals in the decomposition of allyl cyanide

$$CH_2{=}CH{-}CH_2CN \rightarrow CH_2{=}CH^{\bullet} + CH_2CN^{\bullet} \qquad (6a)$$
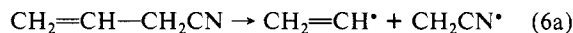
constitute major initiation reactions for both the nitrogen-containing species and the decomposition products without nitrogen.

Benzene (not shown in the product distribution because of its small concentration) is formed only at high temperatures and in very small quantities. The radical $C_3H_3^{\bullet}$ which is produced by an abstraction of a hydrogen atom from both allene and propyne has been suggested to dimerize with the formation of benzene.

b. Products with Bound Nitrogen. In addition to the production of isomerization products, molecules containing nitrogen which result from decomposition processes are also present in the postshock mixtures. Acetonitrile, acrylonitrile, ethyl cyanide, and cyanoacetylene are found in measurable quantities. Some additional products (not shown in the product distribution) C_6H_5CN, $C_6H_5CH_2CN$, $CH_2{=}C{=}CHCN$, and $CH_3C\equiv C{-}CN$ appear only at high temperatures and in very small or trace quantities.

The production of these nitrogen-containing fragment molecules is initiated by the radicals $CH^{\bullet}{=}CHCN$ (produced in reaction 1), $CH_2CN^{\bullet}$ (produced in reaction 6a), and $CH^{\bullet}{=}CH{-}NH^{\bullet}$ (produced in reaction 4). The species $CH_2CN^{\bullet}$ will abstract or recombine with a hydrogen atom to yield acetonitrile whereas $CH^{\bullet}{=}CHCN$ can form either acrylonitrile by abstraction or recombination with a hydrogen atom (similar to $CH_2CN^{\bullet}$) or cyanoacetylene by the loss of a hydrogen atom.[18]

The species $CH^{\bullet}{=}CH{-}NH^{\bullet}$ can either isomerize to acetonitrile by successive 1,2 H atom migrations, or alternatively isomerize to ketene imine, $CH_2{=}C{=}NH$, by a single H atom migration. A similar process in furan where the biradical $CH^{\bullet}{=}CH{-}O^{\bullet}$ isomerizes to ketene, $CH_2{=}C{=}O$, has been established.[1] The fact that the concentration of acetylene in the postshock mixtures is considerably higher than that of acetonitrile

(15) Lifshitz, A.; Frenklach, M.; Burcat, A. *J. Phys. Chem.* **1975**, *79*, 1148.
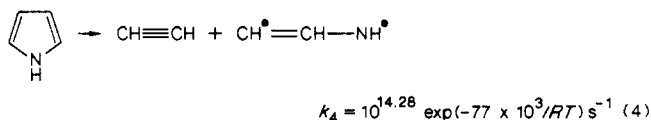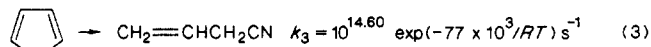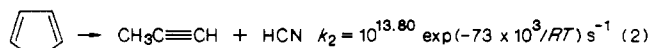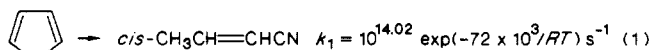(16) Burcat, A. *Fuel* **1975**, *54*, 87.

(17) Lifshitz, A.; Frenklach, M.; Burcat, A. *J. Phys. Chem.* **1976**, *80*, 2437.
(18) Metcalfe, E.; Booth, D.; McAndrew, H.; Woolley, W. D. *Fire Mater.* **1983**, *7*, 185.
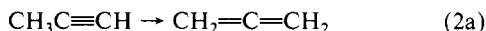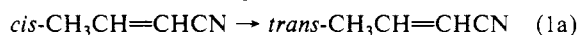
indicates that the isomerization of $CH^\bullet=CH-NH^\bullet$ to acetonitrile is not the dominant route for its stabilization. On the other hand we could not find ketene imine in the postshock mixtures but suspect that, similar to ketene, ketene imine is a very reactive material and cannot be easily analyzed. The inability to analyze ketene imine can explain the partial imbalance of nitrogen atoms compared to four carbon atoms as can be seen in Figure 3.

The Pyrolysis Mechanism. The following scheme of reactions describes the overall pyrolysis mechanism of pyrrole. It is divided into categories such as initiation reactions, isomerizations and decompositions of initial products, and subsequent reactions among the products.
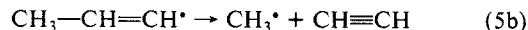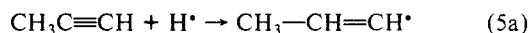
Initiation

$$\text{[pyrrole]} \rightarrow cis\text{-}CH_3CH=CHCN \quad k_1 = 10^{14.02} \exp(-72 \times 10^3/RT)\,s^{-1} \quad (1)$$

$$\text{[pyrrole]} \rightarrow CH_3C\equiv CH + HCN \quad k_2 = 10^{13.80} \exp(-73 \times 10^3/RT)\,s^{-1} \quad (2)$$

$$\text{[pyrrole]} \rightarrow CH_2=CHCH_2CN \quad k_3 = 10^{14.60} \exp(-77 \times 10^3/RT)\,s^{-1} \quad (3)$$

$$\text{[pyrrole]} \rightarrow CH\equiv CH + CH^\bullet=CH-NH^\bullet$$
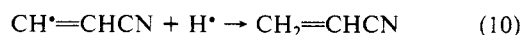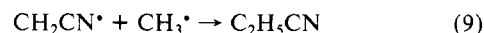
$$k_4 = 10^{14.28} \exp(-77 \times 10^3/RT)\,s^{-1} \quad (4)$$

Isomerization of initiation products

$$cis\text{-}CH_3CH=CHCN \rightarrow trans\text{-}CH_3CH=CHCN \quad (1a)$$

$$CH_3C\equiv CH \rightarrow CH_2=C=CH_2 \quad (2a)$$

Decomposition of initiation products

$$CH_3C\equiv CH \rightarrow CH_2^\bullet-C\equiv CH + H^\bullet \quad (2b)$$

$$2CH_2^\bullet-C\equiv CH \rightarrow C_6H_6 \quad (2c)$$

$$CH_3C\equiv CH + H^\bullet \rightarrow CH_3-CH=CH^\bullet \quad (5a)$$

$$CH_3-CH=CH^\bullet \rightarrow CH_3^\bullet + CH\equiv CH \quad (5b)$$

$$CH_2=CH-CH_2CN \rightarrow CH_2=CH^\bullet + CH_2CN^\bullet \quad (6a)$$

$$CH_2=CH^\bullet \rightarrow CH\equiv CH + H^\bullet \quad (6b)$$

$$2CH_2=CH^\bullet \rightarrow C_4H_6 \quad (6c)$$

$$CH_3CH=CHCN \rightarrow CH_3^\bullet + CH^\bullet=CHCN \quad (1b)$$
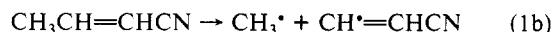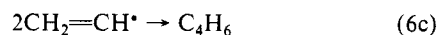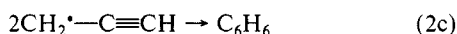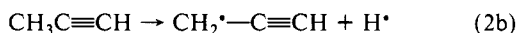
Reactions of unstable intermediates containing bound nitrogen

$$CH_2CN^\bullet + RH \rightarrow CH_3CN + R^\bullet \quad (7)$$

$$CH_2CN^\bullet + H^\bullet \rightarrow CH_3CN \quad (8)$$

$$CH_2CN^\bullet + CH_3^\bullet \rightarrow C_2H_5CN \quad (9)$$

$$CH^\bullet=CHCN + H^\bullet \rightarrow CH_2=CHCN \quad (10)$$

$$CH^\bullet=CHCN \rightarrow CH\equiv C-CN + H^\bullet \quad (11)$$

$$2CH^\bullet=CHCN \rightarrow CH_2=CHCN + CH\equiv C-CN \quad (12)$$

$$CH^\bullet=CH-NH^\bullet \rightarrow CH_3CN \ (?) \quad (13)$$

$$CH^\bullet=CH-NH^\bullet \rightarrow CH_2=C=NH \quad (14)$$
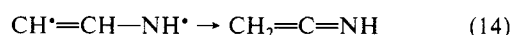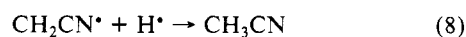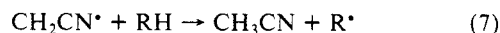
Reactions leading to stable molecules without bound nitrogen
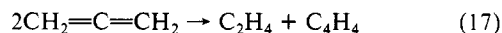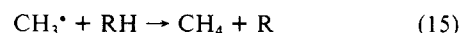
$$CH_3^\bullet + RH \rightarrow CH_4 + R \quad (15)$$

$$2CH_3^\bullet \rightarrow C_2H_6 \quad (16)$$

$$2CH_2=C=CH_2 \rightarrow C_2H_4 + C_4H_4 \quad (17)$$

Registry No. Pyrrole, 109-97-7.

Effect of Iridium(IV) Oxides on the Decay of Zinc Tetrakis(N-methylpyridinium-4-yl)porphyrin π-Radical Cation in the Presence of Poly(styrenesulfonate)

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The π-radical cation of zinc tetrakis(N-methylpyridinium-4-yl)porphyrin (ZnTMPyP^{5+}) has been produced by pulse radiolysis, and its decay reactions have been followed in the presence of oxoiridium(IV) hydrate species and a negatively charged polyelectrolyte, poly(styrenesulfonate) (PSS). The iridium oxide species were produced from hexachloroiridate, and the nature of the product strongly depended on the pH during preparation. A hexahydroxoiridate species that was produced at high pH was found to be very reactive, and its reactions account for most decay processes observed. γ-Radiolysis experiments suggest that this decay involves oxidation of the iridium species in a catalytic process. PSS-stabilized IrO$_x$ hydrosols did not react with the radical cation fast enough to compete with its disproportionation, although such hydrosols were highly reactive when stabilized with neutral or positively charged polymers. The lack of reactivity is attributed to the low mobility of the positively charged porphyrin in the domain of the negatively charged polyelectrolyte as well as to the absence of interpolymer processes. However, under γ-radiolysis conditions, a redox reaction between the hydrosols and the radical becomes feasible.

Introduction

Zinc tetrakis(N-methylpyridinium-4-yl)porphyrin (ZnTMPyP^{4+}) possesses some photophysical[1] and redox[2] properties

that make it a promising photosensitizer for water cleavage systems. However, water photooxidation experiments using ZnTMPyP^{4+} as photosensitizer suffer from reduced efficiency due

(1) (a) Harriman, A.; Porter, G.; Richoux, M.-C. *J. Chem. Soc., Faraday Trans. 2*, **1981**, *77*, 833. (b) Kalyanasundaram, K.; Neumann-Spallart, M. *J. Phys. Chem.* **1982**, *86*, 5163.

(2) (a) Neuman-Spallart, M.; Kalyanasundaram, K. *Z. Naturforsch., B* **1981**, *36*, 596. (b) Harriman, A.; Porter, G.; Walters, P. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 1335.