Photolysis of Pyrrole Vapor at 2139 Å and Room Temperature

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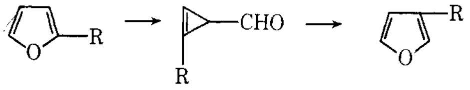
Abstract: The photolysis of pyrrole by radiation with 2139 Å was investigated at room temperature over a pressure range from 0.05 to 4.7 Torr. The products observed were CH_3CCH, CH_2CCH_2, C_2H_2, C_2H_4, H_2, CH_4, C_3H_6, HCN, and polymer. The first five products were initial products of the reaction. Presumably HCN is also an initial product, but CH_4 and C_3H_6 were secondary products resulting from the reaction of hydrogen atoms with C_3H_4 compounds. By introducing NO and O_2 into the reaction system, it was shown that the C_3H_4 compounds, acetylene, and about one-third of the H_2 were produced by molecular elimination. The C_2H_4 and most of the H_2, as well as the secondary products, were produced from free-radical precursors. A detailed mechanism is proposed.

A number of photorearrangements of substituted five-membered heterocycles have been reported.[1–15] The mechanism of photoisomerization of furan derivatives can be explained by ring contraction.[2–8] In the case of thiophenes, an alternative mechanism was suggested involving valence expansion of the sulfur atom to form a valence tautomer intermediate.[9–12] However, the cyclopropenyl thioketone has been isolated recently in the photolysis of tetra(trifluoromethyl)thiophene,[13] so that both mechanisms may be operative. With pyrroles the only report of a 2 → 3 isomerization is with cyanopyrrole.[15]



Photochemical decomposition also occurs in furans, thiophenes, and pyrroles. Srinivasan[16] reported that the photosensitization of furan with Hg-6($^3P_1$) gave carbon monoxide and cyclopropene as the principal products, whereas the direct photolysis[17] produced CO, allene, methylacetylene, and only a trace of cyclopropene.

The photolysis of thiophene vapor was examined both by direct irradiation and by Hg sensitization.[18] In addition to allene and methylacetylene, the products included acetylene, CS_2, vinylacetylene, and polymer. The CS_2 came from CS as a precursor, and vinylacetylene production resulted from the interaction of two thiophene molecules. However, at least part of the acetylene came from photoelimination.

The photochemistry of pyrrole has received little attention. Mullen and Orloff[19] reported that no evidence of photodecomposition was found during their study of the ultraviolet spectrum of pyrrole vapor. However, in the flash photolysis of pyrrole, Callear and Lee[20] observed a free radical which they identified as $CH_2CHCHCN$ because of the similarity of its absorption spectrum with that of the radical produced in the flash photolysis of allyl cyanide (CH_2CHCH_2CN) and crotyl nitrile ($CH_3CHCHCN$).

In this paper we explore the primary photochemical processes in pyrrole vapor at 2139 Å and room temperature.

Experimental Section

Pyrrole (Chemical Procurement Laboratories, Inc.) was purified by gas chromatography on a 20-ft long column packed with 10% tricresyl phosphate on Chromosorb G. The column temperature was 100° with helium as the carrier gas at a flow rate of 60 cm^3/min. All gases were from the Matheson Co. HBr was distilled *in vacuo* at −130° and NO was distilled *in vacuo* at −186° after degassing at −196°. Extra dry grade O_2 and C.P. grade C_2H_4 were introduced into the reaction cell directly.

A cylindrical (50 × 100 mm) quartz cell was used for all runs. It was incorporated into a grease-free vacuum system which utilized Teflon stopcocks with Viton "O" rings. All experiments were run at room temperature. Pyrrole pressures were measured on a Pace P7D transducer gauge. A Phillips type 93106 E/ZN zinc resonance lamp was used as the radiation source. The photochemically effective emission of this lamp is the spectral line at 2139 Å.

The products were analyzed by gas chromatography using a Gow Mac 40-05D voltage regulator with a thermistor detector. Samples of the products were obtained from the gas chromatographic effluent and identified on a MS-9 mass spectrometer. Further identification came from comparison of the gas-chromatographic retention times of the products with authentic commercial samples. A 20-ft long column packed with 10% dimethyl sulfolane on Chromosorb P was operated at 0° with a He flow rate of 30 cm^3/min for quantitative analysis of methylacetylene, allene, acetylene, and propylene. A 10-ft long column packed with Porapak-Q was used for quantitative analysis of ethylene and methane with a He flow rate of 30 cm^3/min at room temperature.

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Table I. Photolysis of Pyrrole at 2139 Å and Room Temperature

[Py], Torr	$I_a \times 10^{-12}$, quanta/(cm^3 sec)	Irradiation time, min	$\Phi\{CH_3CCH\}$	$\Phi\{CH_2CCH_2\}$	$\Phi\{C_2H_2\}$	$\Phi\{C_3H_6\}$
0.05	2.52	20	0.0318	0.0110	0.0100	0.0027
0.06	2.68	20	0.0216	0.0096	0.0097	0.0043
0.09	3.87	20	0.0232	0.0087	0.0088	0.0041
0.09	3.87	20	0.0288	0.0100	0.0126	0.0046
0.09	1.29	20	0.0316	0.0130		0.0009
0.10	0.52	160	0.0263	0.0095	0.0103	0.0039
0.11	0.32	300	0.0213	0.0074	0.0099	0.0028
0.12	4.57	20	0.0235	0.0090	0.0084	0.0029
0.14	5.10	20	0.0237	0.0093	0.0082	0.0035
0.16	5.54	20	0.0257	0.0099	0.0119	0.0039
0.25	7.00	20	0.0254	0.0113	0.0068	0.0035
0.27	7.10	20	0.0293	0.0115	0.0111	0.0048
0.44	8.40	20	0.0263	0.0115	0.0065	0.0039
0.46	8.95	20	0.0275	0.0120	0.0086	0.0049
0.62	9.30	20	0.0300	0.0130	0.0069	9.0035
1.02	10.20	20	0.0282	0.0133	0.0064	0.0025
0.98	4.50	20	0.0321	0.0145		0.0017
1.10	3.40	20			0.0065	0.0015
1.00	1.55	20	0.0322	0.0134		0.0005
1.02	1.39	20			0.0067	0.0009
1.00	0.78	20	0.0339	0.0145		0.0003
1.02	1.39	160	0.0329	0.0160	0.0069	0.0046
0.98	0.85	300	0.0221	0.0143	0.0063	0.0041
1.57	10.90	20	0.0299	0.0133	0.0051	0.0020
1.72	10.90	20	0.0270	0.0109	0.0042	0.0012
2.32	10.90	20	0.0270	0.0133	0.0041	0.0011
3.68	11.50	20	0.0247	0.0116	0.0031	0.0006
4.71	11.50	20	0.0210	0.0116	0.0029	0.0004

This column was also used for H_2 analysis with argon as the carrier gas at 0°.

Since polymer formation was observed during long irradiations, air was admitted to the cell and then heated with an oxygen torch to remove polymer after each run.

HBr was used as an actinometer[21] (where $\Phi\{H_2\} = 1.00$ at 2139 Å for conversions below 1%) for the measurement of quantum yields of the gaseous products. Equal optical densities of reagent and actinometer gases were used to avoid errors due to the uncertain path length of light. Room temperature extinction coefficients (to base 10) at 2139 Å were found on a Cary 15 spectrophotometer to be 0.280 Torr^{-1} cm^{-1} for pyrrole and 5.5×10^{-3} Torr^{-1} cm^{-1} for HBr.

Results

The main products of the photolysis are methylacetylene (CH_3CCH), allene (CH_2CCH_2), ethylene, hydrogen, and acetylene. Small quantities of methane and propylene were also formed. A careful search was made for N_2 and C_2N_2, but they were not found as products. Our chromatographic procedure was unsuitable for determining HCN. However, if the Porapak-Q column was heated to 50° and the flow rate of He increased to 100 cm^3/min, as it was for a few runs, HCN was found. Such an analytical scheme was not useful for quantitative studies because the HCN and CH_3CCH chromatogram peaks had similar retention times and overlapped each other. Thus quantum yields of HCN were not measured. The formation of polymer could be easily observed after 1-hr irradiation. Identification of this polymer has not been done. It is insoluble in organic solvents, acid, and base. Traces of methylacetylene, allene, and acetylene were shown on gas chromatograms after irradiating this polymer for 24 hr.

The quantum yields of products, except for HCN and the polymer, were obtained. To measure the products, separate experiments were run because different columns and different carrier gases were used for gas chromatographic analysis. The product analysis in any run was for either the C_3H_4 products, C_2H_2 and C_3H_6, or CH_4 and C_2H_4, or H_2. The quantum yields of methylacetylene, allene, acetylene, ethylene, and hydrogen decrease as reaction time increases. Since the deposition of polymer on the front window was observed, two sets of actinometer runs were done before and after a 20- and a 120-min irradiation of 1.0 Torr of pyrrole; the light intensity dropped by 25 and 45%, respectively. Therefore, we believe that the time dependence of the quantum yields of CH_3CCH, CH_2CCH_2, C_2H_2, C_2H_4, and H_2 was due essentially to the diminishing intensity as polymer deposits on the window. Taking into account the experimental uncertainty in the analysis of small amounts of products, the ratios, $\Phi\{CH_2CCH_2\}/\Phi\{CH_3CCH\}$ and $\Phi\{C_2H_2\}/\Phi\{CH_3CCH\}$ are essentially independent of the irradiation time as shown in Figure 1. However, the ratio $\Phi\{C_3H_6\}/\Phi\{CH_3CCH\}$ exhibits a pronounced time dependence and rises as the irradiation time is lengthened. Thus C_3H_6 is a secondary product. $\Phi\{CH_4\}$ also does not drop as the duration of irradiation is increased. In fact its time dependence parallels that of C_3H_6, so it too is a secondary product.

Tables I and II give the results of the photolysis of pyrrole as a function of pressure and absorbed light intensity, I_a. The 20-min runs were of short enough irradiation time so that the quantum yields of the primary products are close to their true initial yields, as verified by the two time studies included in Table I. There is no noticeable intensity effect on the primary products, but the quantum yields of C_3H_6 rise noticeably with absorbed intensity for a given pressure and irradiation time, as expected for a secondary product. For the 20-min runs, the quantum yields of methylacetylene

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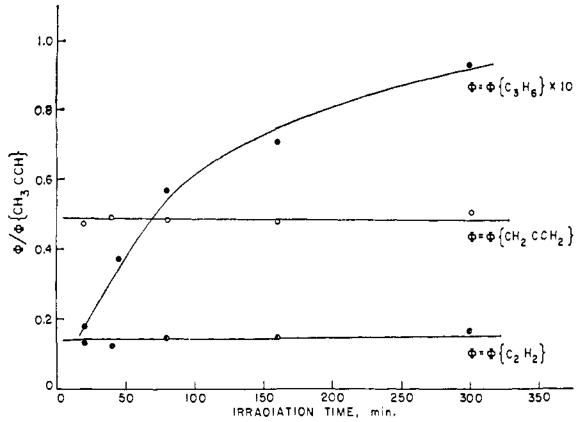


Figure 1. Plots of relative quantum yields of products (relative to CH_3CCH) *vs.* the irradiation time for the photolysis of pyrrole at 2139 Å and room temperature; [Py] = 4.67 Torr, $I_a \simeq 11 \times 10^{12}$ quanta/(cm^3 sec).

and allene initially rise a little and then go down very slowly with increasing pressure. This indicates a weak collisional deactivation in the pressure range larger than 1.0 Torr. When the pressure of pyrrole is low, the secondary processes become important, and CH_4 and C_3H_6 are formed at the expense of CH_3CCH and CH_2CCH_2. Acetylene and hydrogen show a strong inverse pressure dependence. $\Phi\{C_2H_4\}$ is constant at higher pressure, but it goes up rapidly when the pressure drops to less than 0.5 Torr. This is probably due to secondary processes that produce additional ethylene (at least in part from the hydrogenation of acetylene).

Table II. Photolysis of Pyrrole at 2139 Å and Room Temperature for an Irradiation Time of 20 Min

[Py], Torr	$I_a \times 10^{-12}$, quanta/(cm^3 sec)	$\Phi\{CH_4\}$	$\Phi\{C_2H_4\}$	$\Phi\{H_2\}$
0.11	2.90	0.0047	0.0277	0.0294
0.15	3.92			0.0260
0.25	5.91	0.0030	0.0168	
0.32	6.13			0.0193
0.50	6.99			0.0154
0.52	6.99	0.0020	0.0144	
0.75	8.00			0.0140
0.76	8.00	0.0021	0.0147	
0.96	8.50			0.0152
0.99	8.50			0.0180
1.00	8.60	0.0016	0.0147	0.0172
1.49	8.87			0.0128
1.97	9.14			0.0103
1.99	9.14	0.0021	0.0124	
2.50	9.14			0.0084
2.88	9.14			0.0082
2.99	9.14	0.0019	0.0142	
3.90	9.14			0.0068

Table III. Photolysis of Pyrrole in the Presence of Foreign Gases[a]

[X], Torr	$\Phi\{CH_3CCH\}$	$\Phi\{CH_2CCH_2\}$	$\Phi\{C_2H_2\}$	$\Phi\{C_3H_6\}$
	X = O_2, I_a = 10.2×10^{12} quanta/(cm^3 sec)			
0.00	0.0282	0.0133	0.0064	0.0025
0.01	0.0239	0.0107	0.0045	0.0018
0.77	0.0196	0.0092	0.0041	0.0
2.12	0.0195	0.0095	0.0057	0.0
3.0	0.0141	0.0060	0.0046	0.0
	X = NO, I_a = 8.6×10^{12} quanta/(cm^3 sec)			
0.0	0.0380	0.0179		
0.12	0.0323	0.0162	0.0073	0.0011
0.23	0.0320	0.0154	0.0060	0.0
8.2	0.0375	0.0179	0.0075	0.0

[a] [Py] = 1.0 Torr; irradiation time = 20 min.

Table IV. Photolysis of Pyrrole in the Presence of Foreign Gases[a]

[X], Torr	$\Phi\{CH_4\}$	$\Phi\{C_2H_4\}$
0.0	0.0016	0.015
0.34[b]	0.0005	0.0036
0.87[b]	0.0008	0.0013
0.82[c]	0.0009	0.0013

[a] [Py] = 1.0 Torr, irradiation time = 20 min, I_a = 8.6×10^{12} quanta/(cm^3 sec). [b] X = O_2. [c] X = NO.

Table V. Photolysis of Pyrrole in the Presence of Foreign Gases[a]

[X], Torr	$\Phi\{H_2\}$
X = O_2	
0.0	0.0172
0.08	0.0100
0.12	0.0092
0.30	0.0062
0.85	0.0057
1.15	0.0055
1.45	0.0072
1.90	0.0055
X = NO	
0.0	0.0180
0.08	0.0100
0.27	0.0117
0.46	0.0135
0.64	0.0207
1.00	0.0230
2.08	0.0341
X = C_2H_4	
1.83	0.0048
15.0	0.0031

[a] [Py] = 1.0 Torr, irradiation time = 20 min, I_a = 8.6×10^{12} quanta/(cm^3 sec).

In an attempt to obtain further information on the mechanism of this photodecomposition, nitric oxide, oxygen, and ethylene were introduced into the reaction system. The results are given in Tables III–V. Nitric oxide has no effect on the quantum yield of methylacetylene, allene, and acetylene, but inhibits the formation of methane, ethylene, and propylene. This demonstrates that the former three products were formed through intramolecular photodecomposition processes and the latter three products were formed from radical precursors. Oxygen diminished all the quantum yields: CH_3CCH, CH_2CCH_2, C_2H_2, and CH_4 slightly, but C_2H_4 and C_3H_6 markedly. This gives further confirmation for the radical mechanism. The formation of molecular hydrogen is inhibited by oxygen, but is first reduced and then enhanced as nitric oxide is added. Two runs were done with added ethylene in the reaction system. They exhibit the inhibition effect too. However, hydrogen could not be eliminated completely. From the above results, the mechanism of hydrogen formation probably involves hydrogen atoms, but a less important molecular process must also be involved. The initial inhibition of H_2 formation by NO conforms to this view, but the enhancement as more NO is added does not. Perhaps the enhancement comes from the direct absorption of NO at 2139 Å which can then sensitize the decomposition of pyrrole to produce H_2 in a molecular elimination step. Additional products were also found when the inhibiting gases were present. With O_2 added, CO_2 was produced. With NO added, N_2O and trace amounts of vinylacetylene were formed. The vinylacetylene might also arise from NO photosensitization of pyrrole.

Discussion

In order to account for the products, the following primary processes are postulated

$$\mathrm{Py} + h\nu \longrightarrow \mathrm{Py}^* \tag{1}$$

$$\mathrm{Py}^* + \mathrm{M} \longrightarrow \mathrm{Py} + \mathrm{M} \tag{2}$$

$$\mathrm{Py}^* \longrightarrow \mathrm{CH_3CCH} + \mathrm{CNH} \longrightarrow \mathrm{HCN} \tag{3a}$$

$$\longrightarrow \mathrm{CH_2CCH_2} + \mathrm{CNH} \longrightarrow \mathrm{HCN} \tag{3b}$$

$$\longrightarrow \mathrm{C_2H_3}\cdot + \mathrm{C_2H_2N} \tag{3c}$$

$$\longrightarrow \mathrm{I} \tag{3d}$$

$$\longrightarrow \mathrm{Py}\ (+\ h\nu) \tag{3e}$$

where Py stands for pyrrole and Py* is the excited singlet state. Reaction 2 is responsible for the weak pressure dependence of methylacetylene and allene, and reaction 3e is postulated to account for the low total quantum yield. As the formation of methylacetylene and allene was not inhibited by radical scavengers, reactions 3a and 3b are suggested. Reaction 3c is the precursor to C_2H_4 formation. A free radical is needed to explain the inhibition of ethylene formation by oxygen and nitric oxide. To explain the strong pressure dependence on the quantum yields of acetylene and hydrogen, the formation of an intermediate I is considered as one of the primary processes.

The intermediate I is neither the triplet which should be scavenged by oxygen and nitric oxide, nor a ring-contracted intermediate which should be responsible for C_3 formation. Three decay processes of I are postulated as follows

$$\mathrm{I} \longrightarrow \mathrm{C_2H_2} + \mathrm{C_2H_3N} \tag{4a}$$

$$\longrightarrow \mathrm{Py}\cdot + \mathrm{H} \tag{4b}$$

$$\mathrm{I} + \mathrm{M} \longrightarrow \mathrm{Py} + \mathrm{M} \tag{4c}$$

where Py· could be either a cyclic or linear radical. This kind of radical has been detected by Callear and Lee.[20] The formation of hydrogen atoms is needed to explain the production of H_2 and the secondary products which come mainly from free-radical precursors. Some molecular H_2 is also produced in a primary process since none of the radical scavengers could completely eliminate its formation.

To complete the mechanism of the formation of all the compounds observed, the following steps are suggested

$$\mathrm{C_2H_3}\cdot + \mathrm{RH} \longrightarrow \mathrm{C_2H_4} + \mathrm{R} \tag{5}$$

$$\mathrm{H} + \mathrm{RH} \longrightarrow \mathrm{H_2} + \mathrm{R} \tag{6a}$$

$$\mathrm{H} + \mathrm{CH_3CCH} \longrightarrow \mathrm{CH_3CHCH}\cdot \tag{6b}$$

$$\mathrm{H} + \mathrm{CH_2CCH_2} \longrightarrow \mathrm{CH_2CHCH_2}\cdot \tag{6c}$$

$$\mathrm{CH_3CHCH}\cdot \longrightarrow \mathrm{CH_3}\cdot + \mathrm{C_2H_2} \tag{7a}$$

$$\mathrm{CH_3CHCH}\cdot + \mathrm{RH} \longrightarrow \mathrm{C_3H_6} + \mathrm{R} \tag{7b}$$

$$\mathrm{CH_2CHCH_2}\cdot + \mathrm{RH} \longrightarrow \mathrm{C_3H_6} + \mathrm{R} \tag{8}$$

$$\mathrm{CH_3}\cdot + \mathrm{RH} \longrightarrow \mathrm{CH_4} + \mathrm{R} \tag{9}$$

where RH could be pyrrole, the hydrogen atom, or the C_2H_3 radical. Reaction 7a probably occurs from the initially formed $CH_3CHCH\cdot$ radical which still contains its formation energy which is more than sufficient to overcome the decomposition barrier. The fates of C_2H_2N, Py·, and C_2H_3N are not clear. In all likelihood, these fragments should all be incorporated into the polymer eventually.

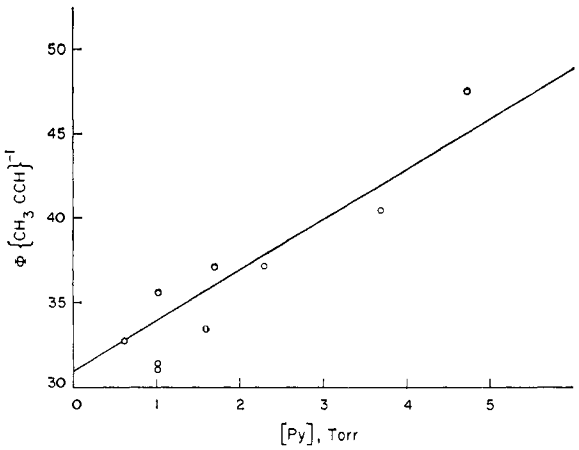


Figure 2. Plots of $\Phi\{CH_3CCH\}^{-1}$ *vs.* the pyrrole pressure in the photolysis of pyrrole at 2139 Å and room temperature for irradiation times of 20 min.

From the mechanism postulated above, quantitative results can be obtained. The quantum yield of methylacetylene should obey the equation

$$\Phi\{\mathrm{CH_3CCH}\}^{-1} = k_3/k_{3a} + k_2[\mathrm{M}]/k_{3a} \tag{I}$$

where $k_3 = k_{3a} + k_{3b} + k_{3c} + k_{3d} + k_{3e}$. A plot of $\Phi\{CH_3CCH\}^{-1}$ *vs.* [Py] is given in Figure 2. The low-pressure results are not included because of the complex secondary effects. The plot is linear, and from the intercept of this plot, we get a value of 31 for k_3/k_{3a}. k_2/k_{3a} corresponds to the slope which has a value of 3.0 Torr^{-1}.

This mechanism also predicts the following relationships for the approximation that the secondary processes are not important.

$$\Phi\{\mathrm{CH_2CCH_2}\}/\Phi\{\mathrm{CH_3CCH}\} = k_{3b}/k_{3a} \tag{II}$$

$$\Phi\{\mathrm{C_2H_4}\}/\Phi\{\mathrm{CH_3CCH}\} = k_{3c}/k_{3a} \tag{III}$$

$$\Phi\{\mathrm{CH_3CCH}\}/\Phi\{\mathrm{C_2H_2}\} = k_{3a}(k_{4a} + k_{4b})/k_{3d}k_{4a} + k_{3a}k_{4c}[\mathrm{M}]/k_{3d}k_{4a} \tag{IV}$$

$$\Phi\{\mathrm{CH_3CCH}\}/\Phi\{\mathrm{H_2}\} = k_{3a}(k_{4a} + k_{4b})/k_{3d}k_{4b} + k_{3a}k_{4c}[\mathrm{M}]/k_{3d}k_{4b} \tag{V}$$

Values for the left-hand sides of the above four equations are listed as a function of the pyrrole pressure in Table VI. Values of the left-hand sides of eq II and III are independent of pressure as expected. They correspond to the ratios of k_{3b}/k_{3a} and k_{3c}/k_{3a}, respectively. Values for the left-hand sides of eq IV and V increase with pressure and are plotted *vs.* [Py] in Figure 3. The plots are reasonably linear with a slope of 1.10 Torr^{-1} and an intercept of 3.7 for the upper line and a slope of 0.62 Torr^{-1} and an intercept of 1.45 for the lower line. The ratio of slope to intercept for both lines should give $k_{4c}/(k_{4a} + k_{4b})$, and this ratio is computed to be 0.30 and

Table VI. Pressure Dependence of the Ratios of Quantum Yields[a]

[Py], Torr	$\Phi\{CH_2CCH_2\}/\Phi\{CH_3CCH\}$	$\Phi\{C_2H_4\}/\Phi\{CH_3CCH\}$	$\Phi\{CH_3CCH\}/\Phi\{C_2H_2\}$	$\Phi\{CH_3CCH\}/\Phi\{H_2\}$
0.5	0.43	0.54	3.8	1.8
1.0	0.43	0.51	4.8	2.1
1.5	0.43	0.50	5.5	2.4
2.0	0.43	0.52	6.0	2.7
2.5	0.43	0.53	6.4	3.5
3.0	0.43	0.54	7.0	3.4
3.5	0.43	Av 0.52	7.6	3.6
4.0			8.0	3.6

[a] All values are calculated from smooth curves based on the values in Table I.

0.43 $Torr^{-1}$ from the upper and lower plots, respectively. The discrepancy is within the experimental uncertainty. Furthermore, the ratio of the slopes or intercepts of the two graphs should give k_{4b}/k_{4a}. Values of 1.78 and 2.56 are obtained, respectively. Finally, the value of $k_{3d}/k_{3a} = 0.96$ can be obtained from the sum of the reciprocals of the intercepts. The rate constant ratios are summarized in Table VII.

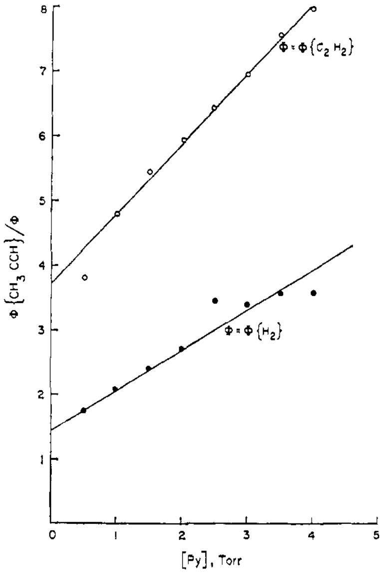


Figure 3. Plots of $\Phi\{CH_3CCH\}/\Phi\{C_2H_2\}$ and $\Phi\{CH_3CCH\}/\Phi\{H_2\}$ *vs.* the pyrrole pressure in the photolysis of pyrrole at 2139 Å and room temperature for irradiation times of 20 min.

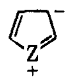
Table VII. Summary of the Ratios of the Rate Constants

Ratio	Value	Unit	Source
k_3/k_{3a}	31	None	Eq 1, Figure 2
k_2/k_{3a}	3.0	$Torr^{-1}$	Eq 1, Figure 2
k_{3b}/k_{3a}	0.43	None	Tables I and VI
k_{3c}/k_{3a}	0.52	None	Table VI
$k_{4c}/(k_{4a} + k_{4b})$	0.30	$Torr^{-1}$	Eq IV, Figure 3
$k_{4c}(k_{4a} + k_{4b})$	0.43	$Torr^{-1}$	Eq V, Figure 3
k_{4b}/k_{4a}	1.78	None	Eq IV and V, Figure 3 (slopes)
k_{4b}/k_{4a}	2.56	None	Eq IV and V, Figure 3 (intercepts)
k_{3d}/k_{3a}	0.96	None	Eq IV and V, Figure 3

At low pyrrole pressures, the step producing hydrogen atoms becomes more important than at higher pressures, and the secondary processes involving hydrogen atom addition become more pronounced. This is easily seen in Table II where $\Phi\{CH_4\}$ and $\Phi\{C_3H_6\}$ rise rapidly for 20-min runs as the pyrrole pressure drops, in spite of the fact that the absorbed intensity is also dropping. Since acetylene is a secondary as well as a primary product, it might be expected that its quantum yield should also rise very rapidly at low pressures too. However, this increase is offset by the removal of acetylene by hydrogen atoms to ultimately produce C_2H_4, and $\Phi\{C_2H_4\}$ shows the marked increase at the low pressure.

It is interesting to compare the products of the photodecomposition of furan, pyrrole, and thiophene. All three give C_3H_4 products, which presumably arise from a ring-contracted cyclopropenylaldehyde intermediate. However, only thiophene and pyrrole produce acetylene. A consideration of the molecular structure of these compounds might help to interpret the formation of their products. The common resonance structure of the five-membered heterocycles with one heteroatom has been considered as follows

A



B

C

where Z can be NH, O, or S. The existence of these structures for the ground electronic state has been confirmed by the dipole moment study of pyrrole derivatives.[22] The degree of delocalization of the electron depends on the electronegativity of the heteroatom, and, therefore, the contribution of the charged structures in the resonance hybrid will be in the following order: thiophene > pyrrole > furan. Presumably the excited electronic state can also be considered to consist of the above structures. Therefore, we use these structures to interpret the formation of the products produced by molecular elimination.

If photon absorption weakens one of the heteroatom carbon bonds, then the results can be explained in terms of the structures A, B, and C. For structure A, the Z(1)–C(2) bond is weakened but the C(3)–C(4) bond is strengthened by resonance. Acetylene cannot be produced, but the cyclopropenyl compound is easily formed and leads to C_3H_4 products.

In the case of structure B, the Z(1)–C(5) bond (numbering is counterclockwise) stability is reduced because of the photon absorbed by the heteroatom, and the C(3)–C(4) bond is weakened due to the accumulation of excess electron density. The C(2)–C(3) bond is also weakened, but it can be stabilized by the hetero-

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[22] H. Kofod, L. E. Sutton, and J. Jackson, *J. Chem. Soc.*, 1467 (1952).

atom through the double bond. Therefore the C(2)–C(3) bond is more stable than the C(3)–C(4) bond. This results in the formation of acetylene from the C(4) and C(5) atoms.

In structure C, the C(2)–C(3) bond is weakened. If this bond breaks, the molecule can either reclose or eliminate C_2H_2 containing the C(3)–C(4) atoms.

Thus, we can argue that furan does not form C_2H_2 because it lacks structure B and possibly C. For pyrrole, structures B and C exist and C_2H_2 is produced though it is less important than the C_3H_4 compounds. With thiophene, structures B and C are even more important, and C_2H_2 is produced in excess of the C_3H_4 compounds.[18]

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Cyclobutadiene and Diphenylcyclobutadiene[1]

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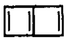
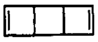
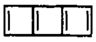
Abstract: Calculations have been carried out using two recently developed semiempirical SCF–MO procedures, one a π approximation and the other (MINDO/2) including all valence electrons, for cyclobutadiene and vicinal diphenylcyclobutadiene. Cyclobutadiene is correctly predicted to have a rectangular singlet ground state with a very low lying triplet, and to be stable to dissociation into acetylene. 1,2-Diphenylcyclobutadiene is correctly predicted to be more stable than the 1,4 isomer by *ca.* 1 kcal/mol; their interconversion, and other properties of cyclobutadiene and diphenylcyclobutadiene, are discussed.

Although the potential theoretical interest of cyclobutadiene (I) has been recognized for a century, this apparently simple molecule until recently resisted all attempts[3] to synthesize it and the key question concerning its possible aromaticity remained unsolved. Five years ago Pettit and his collaborators[4] first prepared cyclobutadiene as a highly reactive intermediate by oxidation of its iron tricarbonyl complex[5] and since then its chemistry has been studied intensively.[6]


I


II


III


IV

Some time ago one of us[7] developed a simple theoretical treatment of organic chemistry based on the application of perturbation theory to the MO approximation; one of the achievements of this PMO method was to provide an apparently very successful account of aromaticity. According to this, I should be not merely not aromatic, but antiaromatic, having a large negative resonance energy; its observed properties are certainly consistent with such a destabilization since it shows reactivity of a different order to any other cyclic polymethine.

While this approach accounts qualitatively for the observed reactivity of I, a number of problems remain that can be solved only by the use of some more quantitative treatment. In particular, it is apparent from simple Hückel theory that I might possess a triplet ground state, and it has also been suggested that the instability of I might be such as to lead to exothermic dissociation into acetylene. The extraordinary ease with which I undergoes Diels–Alder reactions also needs some subtler explanation than one based on the antiaromaticity of I; for the transition state for such a reaction should be isoconjugate[8,9] with bicyclohexatriene (II) which on casual inspection seems likely to be also antiaromatic.

Various MO calculations for I have been reported in recent years;[10] these, however, have been based on approximations which are known to give very poor estimates of heats of atomization and it is therefore impossible to place any reliance on predictions of chemical behavior based on them.[11]

Recent work in these laboratories has, however, led to the development of semiempirical SCF–MO procedures that for the first time give heats of atomization

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(2) Robert A. Welch Postdoctoral Fellow; on leave of absence from the Rudjer Bošković Institute, Zagreb, Croatia, Yugoslavia.

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