ropies in the susceptibilities are caused just as much by anisotropies in the parameters A and B as by the presence of the parameter D. This conclusion agrees with the results of Amos and Roberts.[7] It should be noted, however, that the results of Table II are not as meaningful as the results of Table I. In Table II three parameters are adjusted to represent five experimental results that do not seem very accurate, and the authors feel that the number of experimental values is not sufficiently large for producing a meaningful theoretical description.

Discussion

The idea of deriving a semiempirical description of the diamagnetic susceptibilities of organic molecules is not a new one and the literature on this subject is fairly extensive. Papers by London,[4] Hall and Hardisson,[6] Amos and Roberts,[7] and Gawer and Dailey,[8] are all concerned in particular with aromatic molecules. However, it is felt that the present investigation contains some features that are not contained in the previous theoretical descriptions. The work by London[4] is concerned only with the π electrons and it is fairly well established now that the σ electrons contribute significantly to both the total susceptibilities and to the anisotropies. The other authors who are quoted above attempt to derive semiempirical descriptions of the susceptibilities of aromatics and they all include the σ electrons in their considerations. The main difference between these theories and the present one is that they attempt to express the contributions of the σ electrons in terms of atomic contributions while we express them in terms of the contributions of the localized bonds and of the bond-bond interactions. The authors feel that this representation has the advantage that it can be justified in a more or less rigorous theoretical fashion and, also, that it is more precise than any of the other methods. It should be noted that London's calculation[4] is perhaps less accurate than Hall and Hardisson's, but the present approach uses only the ratios of London's results and it is felt that these ratios are quite accurate.

The results of this paper show how this semiempirical description of diamagnetic susceptibilities[2b] may be extended to conjugated systems. The polyacenes have been treated, as an example, but the formalism developed here is suitable for the description of all types of conjugated molecules. It was shown that in the case of a conjugated molecule, having delocalized molecular orbitals, the diamagnetic susceptibility may be represented as a sum of three parts, χ_Σ, χ_Π, $\chi_{\Sigma\Pi}$. These parts are the contributions of the σ electrons and of the π electrons and a contribution due to σ–π interactions. The parts χ_Σ and $\chi_{\Sigma\Pi}$ are treated in the same fashion as in the authors' theory of saturated molecules. The part χ_Π is derived from London's theory.[4,5] Even though the absolute values of London's theory[4,5] may not be too accurate it is felt that the ratio of these results for different molecules are quite reliable. The satisfactory agreement between our semiempirical susceptibility values and the experimental results seem to support this assumption.

Finally, the authors feel that a combination of the methods described above with the procedures discussed previously[2] constitutes the framework for a general semiempirical description of the diamagnetic susceptibilities of all organic molecules, both saturated and unsaturated.

---

(8) A. H. Gawer and B. P. Dailey, *J. Chem. Phys.*, **42**, 2658 (1965).

Mercury ($^3P_1$) Sensitized Photolysis of 2,5-Dimethylfuran

S. Boué[1] **and R. Srinivasan**

Contribution from the IBM Thomas J. Watson Research Center,
Yorktown Heights, New York 10598. *Received September 15, 1969*

Abstract: The photodecomposition of 2,5-dimethylfuran vapor sensitized by mercury ($^3P_1$) atoms was a complex process in which more than 11 products were formed in characterizable amounts. This number did not include dimeric and condensed materials. The products, in the order of decreasing abundance, were 4-methylcyclopent-2-enone, *cis*- and *trans*-1,3-pentadienes, CO, 1-methyl-3-acetylcyclopropene, hexa-3,4-dien-2-one, 2-ethyl-5-methylfuran, isoprene, 1,3-dimethylcyclopropene, 2-pentyne, and propylene. The formation of 2-ethyl-5-methylfuran was the only process that was totally eliminated on the addition of oxygen. It is hence believed to be the only reaction of free-radical origin. The three minor C_5H_8 products were shown to be formed by the secondary photolysis of the 1,3-pentadienes. The intermediate that leads to 4-methylcyclopent-2-enone and (CO + 1,3-pentadiene) is best rationalized as a carbene while the intermediate that gives the two other isomeric ketones may be a 1,3-diradical. Quantum yields and data on pressure quenching have also been obtained.

In earlier studies on the mercury-photosensitized decomposition of furan[2] and methylfurans[3,4] the most important process was postulated to be a ring contraction to give cyclopropene-3-carboxaldehyde (I). Ullman and Singh[5] had first observed such a

---

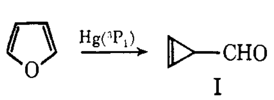
(1) Postdoctoral Fellow, 1968–1970.

(2) R. Srinivasan, *J. Amer. Chem. Soc.*, **89**, 1758, 4812 (1967); *Pure Appl. Chem.*, **16**, 65 (1968).

(3) H. Hiraoka and R. Srinivasan, *J. Amer. Chem. Soc.*, **90**, 2720 (1968).

(4) H. Hiraoka, *J. Phys. Chem.*, **74**, 574 (1970).

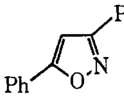
(5) E. F. Ullman and B. Singh, *J. Amer. Chem. Soc.*, **88**, 1844 (1966); **89**, 6911 (1967).



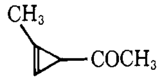
I

(1)

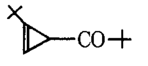
photochemical reaction in the isoxazole system (II). There is considerable evidence to show that this is a general photoreaction for many five-membered heterocyclics.[6] In the furan system, it was surmised that the



II

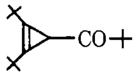


III



IV

V



VI

simple ring-contracted product may be sufficiently stable to be isolable if both the 2 and the 5 positions were suitably substituted. Accordingly, the mercury-photosensitized decomposition of 2,5-dimethylfuran was attempted. The isolation and characterization of the cyclopropene isomer, which in this instance was 1-methyl-3-acetylcyclopropene (III), have been presented.[7] During the course of that work it was found that the sensitized photodecomposition of 2,5-dimethylfuran was a complicated process. We report here on a detailed study of this system.

The photochemistry of other dialkylfurans[8] has recently been reported. Van Tamelen and Whitesides[8] have conducted a study of the photodecomposition of 2,5-di-*t*-butyl-, 2,4-di-*t*-butyl-, and 2,3,5-tri-*t*-butylfurans in solution. They have described the isolation of the cyclopropenylcarbonyl compounds IV, V, and VI. Their work will be alluded to again in a later section.

Experimental Section

Materials. 2,5-Dimethylfuran (Columbia Organic Chemicals) was chromatographed over silica to remove the carbonyl compound which was present as an impurity. It was subsequently distilled on an annular spinning-band column; a narrow cut which boiled at 93.2° (751 Torr) was collected, degassed before use, and stored at −20°. Gas chromatographic analysis showed no detectable impurities in it.

Apparatus. Mercury resonance lamps of the germicidal type were used as light sources. Quantitative studies were conducted in a spherical flask 1078 ml in volume with a central quartz well in which the lamp (2 cm effective length) was placed. The geometry of the system was such that it approximated a point source at the center of a sphere. An annular cavity between the lamp and the flask was kept at 22° by the circulation of deionized water from a constant temperature bath. This served to maintain the temperature of the lamp constant. The lamp was operated through a constant voltage transformer and allowed to warm up for 45 min before photolysis was started. The intensity of the radiation at 253.7 nm which entered the flask was 1.06×10^{17} quanta/sec as measured with a ferrioxalate actinometer.[9] This figure includes a correction for the output of the lamp at wavelengths other than 253.7 nm. All runs were made at the vapor pressure of 2,5-dimethylfuran at 0° which was 13.0 Torr. A drop of mercury was present in the flask.

Analysis. At the end of the photolysis, a known weight of cyclohexane was added to the mixture of volatile products which was trapped at −190°. An aliquot of this sample was injected on a gas chromatographic column of Ucon oil (20% on Chromosorb-8′; F&M Model 500 gas chromatograph). The column was programmed to operate from room temperature to 160° over a 120-min interval. Peak areas were calibrated with authentic samples of the products which were prepared in large-scale photolysis experiments.

Infrared and nmr spectra of the products were measured in carbon tetrachloride solution. For the latter, dioxane or tetramethylsilane was used as an internal reference.

Results

Products. Mercury-sensitized photodecomposition of 2,5-dimethylfuran gave a host of products of which 13 were isolated and 11 were identified. No attempt was made to characterize either dimeric or polymeric products. A yellow liquid polymer was observed on the walls of the reaction vessel at conversions of the order of 40% or more. A consideration of the mass balance suggested that polymer formation took place even at lower conversions.

There were two gaseous products which were identified to be carbon monoxide and propylene. There were five products with the molecular formula C_5H_8 (mol wt by mass spectrometry 68). Three of these were identified as *cis*-1, 3-pentadiene, *trans*-1, 3-pentadiene, and isoprene by comparing their infrared spectra and retention times on a gas chromatographic column with those of authentic material.

The fourth isomer had infrared absorptions at 1770 (C=C) and 1366 cm^{-1} (CH_3). Its nmr spectrum showed absorptions at τ 9.02 (3 H, doublet, J = 4 Hz), 8.66 (1 H, broad), 7.91 (3 H, singlet), and 3.43 (1 H, complex). The presence of only one olefinic proton at a chemical shift of τ *ca.* 3 suggested a cyclopropene structure. Since one methyl appeared to be on a -CH- group and another on a olefinic carbon, the structure 1,3-dimethylcyclopropene would fit all of these observations. The infrared C=C stretching frequency is in agreement with the value given in the literature.[10] The fifth C_5H_8 isomer was identified as 2-pentyne by comparing it with an authentic sample.

The eighth product (in the order in which products streamed from the gas chromatograph) had the formula $C_7H_{10}O$ (mol wt by mass spectroscopy 110). Its infrared spectrum showed an intense absorption peak at 1223 cm^{-1} (C-O-C) and medium absorptions at 1365 (CH_3), 1023, 1005, 953, and 937 cm^{-1} (furan ring). Its ultraviolet spectrum in cyclohexane showed a maximum at 219 nm (ϵ 8000 cm^2 mol^{-1}) and a shoulder at 235 nm. This spectrum was similar to that of 2,5-dimethylfuran. The nmr spectrum consisted of absorptions at τ 8.82 (3 H, triplet, J = 7Hz), 7.80 (3 H, singlet), 7.43 (2 H, quartet, J = 7.5Hz), and 4.31 (2 H, singlet). The five protons at τ 7.43 and 8.82 together fitted an ethyl group. Since the chemical shifts of the two olefinic protons are identical with those of the two β protons in 2,5-dimethylfuran, the structure 2-ethyl-5-methylfuran would fit all these data.

The ninth product proved too unstable for any spectroscopic study. The tenth product was formed only in small yield. Its molecular weight by mass spectrometry was 112. Its infrared spectrum indicated

---

(6) R. Srinivasan, *Pure Appl. Chem.*, in press.

(7) R. Srinivasan, paper presented at the IUPAC Symposium On Organic Photochemistry at Enschede, Holland, July 1967.

(8) E. E. Van Tamelen and T. H. Whitesides, *J. Amer. Chem. Soc.*, **90**, 3894 (1968).

(9) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, New York, N. Y., 1966, p 783. As suggested in this reference, a calibration was performed using a standard solution of $FeSO_4$, $(NH_4)_2SO_4$, and $6H_2O$. The value of ϵ_{510}^{max} 1.104×10^4 cm^2 mol^{-1} was used for the Fe^{2+}:phenanthroline complex.

(10) G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 70 (1967).

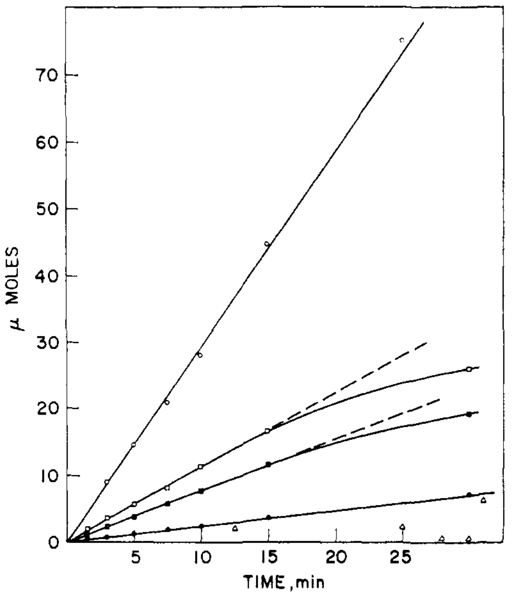


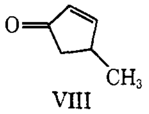
Figure 1. Rates of formation of the major products in the mercury-photosensitized decomposition of 2,5-dimethylfuran: ○, 2,5-dimethylfuran (disappearance); □, 4-methylcyclopent-2-enone; ■, *cis*- and *trans*-1,3-pentadiene; ●, 2-ethyl-5-methylfuran; △, 1-methyl-3-acetylcyclopropene. Multiply ordinate scale by 10^{-1} for 2-ethyl-5-methylfuran.

the possible presence of a carbonyl group (1724 cm^{-1}) and a methyl adjacent to it (1355 cm^{-1}). The ultraviolet spectrum showed intense maxima at 195 and 252 nm. The product was not identified.

There were three products of the formula C_6H_8O (mol wt by mass spectrometry 96) and hence isomeric to the starting material. The first of these had infrared absorptions at 1948 (C=C=C), 1683 (C=O, possibly conjugated), 1382 (CH_3), and 1355 cm^{-1} (CH_3 adjacent to a C=O). The nmr spectrum had absorptions at τ 8.13 (3 H, doublet J = 6Hz), 7.80 (3 H, singlet), 4.37 (1 H, doublet, J = 7Hz), and 4.7 (1 H, complex). The absorption at τ 7.80 could be attributed to the methyl protons in an acetyl group. The protons in the methyl group at τ 8.13 were allylic and coupled to one of the two olefinic protons. These data suggested that the compound was a ketone with an allenic group. The ultraviolet spectrum of the compound in cyclohexane, which contained a maximum at 217.5 nm (ϵ 6500 cm^2 mol^{-1}), was similar to that of the allenic ketone which was described by Van Tamelen and Whitesides.[8] Since the compound rearranged thermally even in the injection port of a gas chromatograph to give 2,5-dimethylfuran as the major product, the carbon skeleton of the latter was probably preserved in the molecule. Hence the structure hexa-3,4-dien-2-one (VII) was assigned to the compound.

$CH_3COCH{=}C{=}CHCH_3$

VII



VIII

The second C_6H_8O isomer was the 1-methyl-3-acetylcyclopropene (III) that was mentioned earlier. Its structure was based on its infrared spectrum (C=C at 1805, C=O at 1690, and CH_3 adjacent to C=O at 1355 cm^{-1}), nmr spectrum (3 H at τ 8.16, singlet; 3 H at τ 7.79, singlet; 1 H at τ 7.82, 1 H at τ 3.59, doublet J = 2 Hz), and ultraviolet spectrum in cyclohexane (λ_{max} 193 nm, ϵ 7500 cm^2 mol^{-1}). Recently, this compound has been synthesized by Monti and Bertrand.[11] Their spectroscopic data agree well with those reported here. Further evidence for the structure of this product was obtained from the fact that on standing in solution at room temperature, it rearranged to a mixture of 2,4- and 2,5-dimethylfurans in the ratio of 2:1.

The third C_6H_8O isomer was the single most important product of the photosensitized decomposition of 2,5-dimethylfuran. Its infrared spectrum showed an intense absorption at 1715 cm^{-1} (C=O) and lesser absorptions at 1660, 1590 (unsaturation), and 1375 cm^{-1}. The ultraviolet spectrum in cyclohexane had a maximum at 213.5 nm (ϵ 8875 cm^2 mol^{-1}). The nmr spectrum showed absorptions at τ 8.81 (3 H, doublet, J = 7 Hz), 8.07 (1 H, doublet, J = 2 Hz), 7.67 (1 H, doublet, J = 6 Hz), ~7 (1 H, complex), 4.01 (1 H, doublet of doublets, J = 6 and 2 Hz), and 2.49 (1 H, doublet of doublets, J = 6 and 2 Hz). Since the compound contained only two olefinic protons and the methyl group was not allylic, a monocyclic structure with one double bond was indicated. The ultraviolet and infrared spectra suggested a conjugated cyclopentenone. The position of the methyl group is presumably C-4 since it is coupled strongly to the proton at τ ~7. This would lead to the structure 4-methylcyclopent-2-enone (VIII). Confirmatory evidence was obtained by hydrogenating the compound in isooctane. It absorbed 1 mol of hydrogen to give a product of mol wt 98. This was identified as 3-methylcyclopentanone on the basis of its infrared spectrum and the melting point of its 2,4-dinitrophenylhydrazone (128.0–128.5°, undepressed on mixing with authentic material).

In a typical run on a preparative scale in which about 50% of the intial amount of 2,5-dimethylfuran had been decomposed, the mass balance (volatile products only) was good to 70%. The photolyzate consisted of the following fractions of the various materials: recovered 2,5-dimethylfuran, 0.75; *trans*-1,3-pentadiene, 0.04; *cis*-1,3-pentadiene, 0.04; isoprene, 1,3-dimethylcyclopropene, and 2-pentyne, <0.01; 2-ethyl-5-methylfuran, 0.01; hexa-3,4-dien-2-one, >0.01; 1-methyl-3-acetylcyclopropene, 0.02; and 4-methylcyclopent-2-enone, 0.12.

Quantitative Studies. The disappearance of 2,5-dimethylfuran and the formation of the major products are plotted as a function of time in Figure 1. Over the linear parts of these plots which correspond to conversions of 8% or less, the following quantum yields were measured: disappearance of 2,5-dimethylfuran, 0.28; *trans* 1,3-pentadiene, 0.04; *cis*-1,3-pentadiene, 0.03; carbon monoxide, 0.08; and 4-methylcyclopent-2-enone, 0.10. At these conversions, the rates of formation of 1,3-dimethylcyclopropene, isoprene, and 2-pentyne were too small to be measured. These compounds were formed at measurable rates only at conversions greater than 10%. Their yields as a function of time are listed separately in Table I.

The effect of added gases on the yields of the various products is given in Table II. The ratios of CO to the 1,3-pentadienes ranged from 1.1 to 1.3. The differences

---

(11) H. Monti and M. Bertrand, *Tetrahedron Lett.*, 1235 (1969).

Table I. Formation of Minor C_5 Products[a]

Time, min	Products, μmol		
	Dimethylcyclopropene	Isoprene	2-Pentyne
12.5	0.03	0.06	
30	0.08	0.17	0.10
45	0.15	0.29	0.15
60	0.19	0.35	0.23

[a] Pressure = 13 Torr, temp = 23°, intensity = 1.06×10^{17} quanta/sec, cell volume = 1078 ml.

from unity were real. The yields of the other C_5 products were quite small when compared to those of the 1,3-pentadienes. The ratio of 4-methylcyclopent-2-enone to the 1,3-pentadienes was 1.4 at 13 mm but increased to 2.0 on the addition of an excess (199 Torr) of CO_2. The ratio was unaffected by the presence of oxygen.

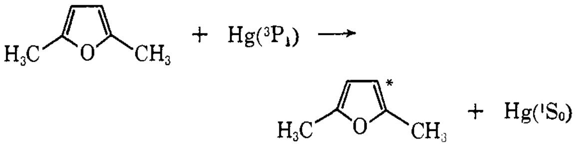
Table II. Effect of Oxygen and Carbon Dioxide on the Yields of Major Products[a]

Time, min	Gas added	Gas pressure, Torr	% conv	Products, μmol				
				trans-1,3-Pentadiene	*cis*-1,3-Pentadiene	Ethylmethylfuran	Methylacetylcyclopropene	4-Methylcyclopent-2-enone
15	None		5.9	6.5	5.4	0.4	2.1	16.5
30	None		11.6	10.7	8.6	0.7	6.3	25.9
15	Oxygen	5.0	5.3	1.8	1.6	0	0.4	5.4
15	Oxygen	9.0	4.6	1.4	1.4	0	0.4	4.2
15	Oxygen	13.8	7.1	0.7	0.6	0	0.1	1.8
30	CO_2	52.0	8.7	5.8	4.5	0.4	0.4	16.7
30	CO_2	92.1	7.7	3.9	3.1	0.2		12.2
30	CO_2	126.3	8.5	2.8	2.1	0.2	0.4	9.7
30	CO_2	198.5	6.2	1.6	1.3	0.1	0.1	5.6

[a] Conditions as in Table I.

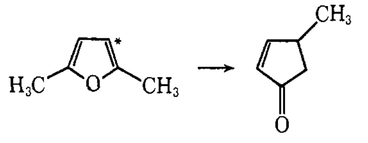
Discussion

The yields of major products of the mercury photosensitized decomposition of 2,5-dimethylfuran, which are 4-methylcyclopent-2-enone and 1,3-pentadiene (+CO), are seen to decrease steadily on the addition of CO_2. This pressure quenching suggests that excited molecules of 2,5-dimethylfuran are formed in this system (reaction 2). A similar pressure dependence (self-quenching as well as quenching by foreign gas molecules) has been well documented in the case of furan itself.[2] If spin is conserved in reaction 2, the excited state of the 2,5-dimethylfuran that is formed will be a triplet.



(2)

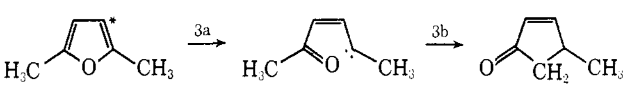
The chemical reactions of the excited 2,5-dimethylfuran seem to follow two major and several minor pathways. The former are reactions 3 and 4. The latter are the processes which lead to 1-methyl-3-acetylcyclopropene, hexa-3,4-dien-2-one, and free-radical products. We shall consider these reactions in order.



(3)

$$\longrightarrow CO + CH_3CH{=}CHCH{=}CH_2 \quad (4)$$

The photoisomerization of 2,5-dimethylfuran to 4-methylcyclopent-2-enone is a novel reaction in that it leads to a carbonyl compound (as photoreactions of vinyl ethers commonly do)[12] but with the same number of atoms in the ring as in the furan. The process is undoubtedly intramolecular as it is not scavenged on the addition of oxygen. The mechanism may involve an initial split of the furan ring to give a carbene which can insert internally on a C–H bond in the methyl group across from it. The possible occurrence of a carbene as an intermediate in the photochemistry of furans has been considered[2] and indirect evidence for its participation has been obtained in furan itself. However, in that instance, the pathway that involved a carbene was of minor importance when compared to the ring contraction reaction 1. In 2,5-dimethylfuran the situation is reversed, in that the carbene leads to the major product(s) while the ring contraction is a comparatively minor process.



It is reasonable to assume that CO and the 1,3-pentadienes are formed in the same decomposition reaction although the former tends to be in slight excess.[13] The overall reaction is a most unusual one as it involves the extrusion of CO to give a linear product with no branching. The failure of oxygen to scavenge these compounds rules out a free-radical pathway. Their rates of formation are quite constant at low conversion which indicates that they are not formed in a secondary reaction. It is unlikely that 4-methylcyclopent-2-enone is involved in this process as its yield, relative to the two 1,3-pentadienes, holds remarkably constant with time without any display of an inflection in the rate curve that would be indicative of two consecutive reactions. But this excludes only a two-photon process and not one in which the ketone is formed (*e.g.*, in (3)) in an excited state and decomposes further. There is a slight increase in the yield of 4-

[12] E. Murad, *J. Amer. Chem. Soc.*, **83**, 1327 (1961).

[13] At high conversions, this is probably due to the loss of some of the 1,3-pentadiene by secondary decomposition. At low conversions, a primary split to give propylene and a C_4H_4O fragment, which in turn can lose CO, may explain this inequality.

methylcyclopent-2-enone, on a relative basis, in the runs carried out in the presence of a large excess of CO_2. This suggests that the triplet state of 2,5-dimethylfuran can yield either the ketone or the pentadiene, depending on its energy content, but the details of the mechanism must await further investigation.

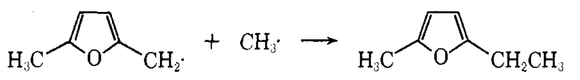
The isolation of 1-methyl-3-acetylcyclopropene represents the simplest furan system (or oxygen-bearing five-membered heterocycle) in which the primary ring contraction product has been identified. It seems clear that in furan itself, it is the reactivity of the product I that causes problems in its isolation. The *t*-butyl substituents used by Van Tamelen and Whitesides[8] do not seem to contribute significantly to the stability of the cyclopropenyl ketone as the yield reported by them is of the same order as that observed here.

The rearrangement of 1-methyl-3-acetylcyclopropene at room temperature to 2,4- and 2,5-dimethylfurans demonstrates that the reverse of reaction 1 can occur thermally as we had postulated.[3] The need for the use of light energy for this reaction in the case of the *t*-butylcyclopropene derivatives[8] and the phenyl-substituted azirine derivatives[5] (to the isoxazole only) may be due to the greater complexity of the molecules involved. This, in turn, would raise the temperature at which the ring expansion occurred at a convenient rate.[14]

The three C_5H_8 products other than the 1,3-pentadienes are clearly secondary products, since (i) their formation is detected only after 4% or more of the 2,5-dimethylfuran had been converted and (ii) their rates of formation actually increase with time while the rates of formation of the major products decrease sharply after about 10% of the 2,5-dimethylfuran had been converted.

Although cyclopropenes are formed in the mercury-sensitized decomposition of furans and methylfurans, their formation involves the migration of an α hydrogen,[2] a process which is blocked by the α-methyl groups in the present example. The most likely source of the minor C_5H_8 products is the secondary photosensitized isomerization of the 1,3-pentadienes. Some preliminary experiments on the irradiation of 1,3-pentadiene vapor with 253.7-nm light in the presence of mercury seem to bear this out. The isoprene may be a tertiary product that is formed from a "hot" 1,3-dimethylcyclopropene since its yield drops to zero at high pressures of 1,3-pentadiene.

2-Ethyl-5-methylfuran is clearly formed by the free-radical process



IX

(5)

since oxygen eliminates this product completely. The radical IX is probably formed by the abstraction of a hydrogen atom from the CH_3 group. The origin of the methyl radical is obscure.

It is a remarkable fact that the photochemical primary processes in molecules which incorporate a furan ring change drastically with even a minor substitution. This is fully confirmed and extended by the present study. The investigation of other dimethylfurans should be of considerable interest.

---

[14] The present results on the thermal isomerization of 1-methyl-3-acetylcyclopropene are at variance with those reported in ref 11. Although these workers used a temperature greater than the ambient temperature to synthesize III, they did not make any reference to the possible formation of 2,4- or 2,5-dimethylfurans. We are unable to explain this discrepancy.

Flash Photolysis of Ozone–Cyanogen Mixtures

Clifford W. Hand[1] and Robert M. Hexter

Contribution from the Mellon Institute and Department of Chemistry,
Carnegie–Mellon University, Pittsburgh, Pennsylvania 15213.
Received June 23, 1969

Abstract: Flash photolysis of C_2N_2–O_3 mixtures gives rise to two unstable products, both of molecular formula C_2N_2O. The one is the symmetrical product of the insertion of $O(^1D)$ into the C–C bond of C_2N_2, while the other results from the terminal addition of $O(^3P)$.

Although the thermochemistry of cyanogen combustion is well known,[2a] the kinetics and mechanism have not received anything like the attention which has been lavished on hydrocarbon combustion kinetics. However, studies of burning velocities of cyanogen–oxygen mixtures[2b] have yielded a value of 35–40 kcal for the activation energy of the overall process $C_2N_2 + O_2 \rightarrow$ products. The earlier work of Thomas, Gaydon, and Brewer[3] has demonstrated the existence in C_2N_2–O_2 flames of CN, C_2, and NO (NH, CH, and OH were also observed and shown to arise from H_2O impurity in the C_2N_2 sample), although the roles of these species in the combustion mechanism were not elucidated.

More recently some of the elementary reactions of cyanogen and the CN radical have been studied by flash photolysis techniques.[4–6] In particular, rate

---

[1] Department of Chemistry, University of Alabama, University, Ala. 35486.

[2] (a) J. B. Conway and A. V. Grosse, *J. Amer. Chem. Soc.*, **80**, 2972 (1958); (b) E. Rutner, K. Scheller, and W. H. McLain, Jr., *J. Phys. Chem.*, **64**, 1891 (1960).

[3] N. Thomas, A. G. Gaydon, and L. Brewer, *J. Chem. Phys.*, **20**, 3 (1952).

[4] N. Basco and R. G. W. Norrish, *Proc. Roy. Soc., Ser. A*, **283**, 291 (1965).