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.

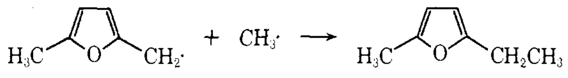
The isolation of 1-methyl-3-acetylcyclopropene represents the simplest furan system (or oxygen-bearing five-membered heterocycle) in which the primary ring contraction product has been identified. It seems clear that in furan itself, it is the reactivity of the product I that causes problems in its isolation. 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.

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[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

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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

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[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).

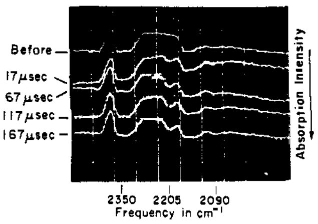

Figure 1. Photolysis of cyanogen–ozone: 0.7 Torr O_3, 5.0 Torr C_2N_2, 19 Torr Ar; LiF prism, 0.5-mm slits, 16.5-m optical path length; flash energy, 1500 J, set off 17 μsec before the second scan; scope, 10 mV/cm, 1 μsec/cm; scan rate, 20.0 kiloscans/sec. The absorption bands in the before scan are due to atmospheric CO_2 (2350 cm^{-1}), C_2N_2 (2149 and 2090 cm^{-1}), and O_3 (2105 cm^{-1}). The post flash absorption at 2205 ± 10 cm^{-1} is due to the transient NCOCN produced in the reaction.

constants have been measured, with varying degrees of accuracy, for the reactions

$$CN + O_2 \longrightarrow NCO + O \qquad (I)^4$$

$$CN + O_2 \longrightarrow CO + NO \qquad (II)^4$$

$$CN + NO \longrightarrow NOCN \qquad (III)^5$$

Since in all probability the reaction of oxygen atoms with the substrate C_2N_2 is important in cyanogen combustion, it is appropriate to study the reaction $O + C_2N_2$ in systems other than flames. In the following, we report the results of the flash photolysis of mixtures of cyanogen and ozone; the results were followed by means of infrared absorption spectroscopy.

Experimental Section

The apparatus for conducting infrared kinetic spectroscopy has been described.[7,8] Briefly, it consists of a rapid scanning ir spectrometer coupled to a flash-photolysis reaction vessel.

The reagents used in this work were, except in the case of ozone, obtained commercially and used without purification: Ar, Linde 99.996%; N_2, Linde HP dry; SF_6, Matheson 98%; C_2N_2, Matheson 98.5%. Ozone was generated in a Welsbach T-23 ozonator and stored at −78° on silica gel.[9] The ozone as delivered to the reaction vessel was not pure but contained several per cent oxygen.

Results

When mixtures of cyanogen and ozone were flash photolyzed a new absorption band was observed in the infrared spectrum at a frequency of 2205 ± 10 cm^{-1}. The band appeared within 20 μsec (Figure 1), built up to maximum intensity in less than 70 μsec, and diminished gradually over the course of several minutes. The mode of decay was second order (Figure 2). When mixtures of cyanogen and oxygen were flashed no changes in the ir absorption spectrum were observed. Photolysis of cyanogen alone did not produce observable amounts of CN radical. This result is in agreement with the work of Morrow and McGrath and is to be expected since cyanogen absorbs only weakly within the transmission limits of ordinary quartz.[10]

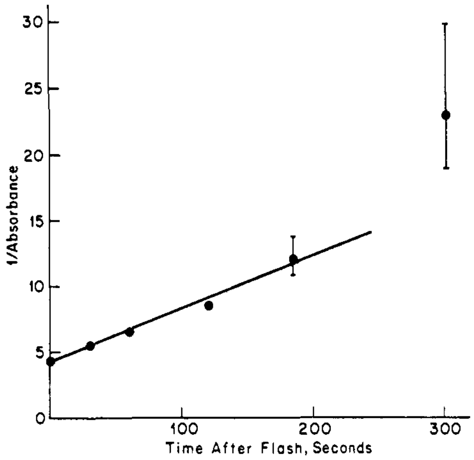

Figure 2. Second-order plot of decrease in absorbance at 2205 cm^{-1}; 1.8 Torr O_3; 6.0 Torr C_2N_2; 47 Torr Ar; flash energy, 1500 J.

The optical density of the 2205-cm^{-1} absorption, measured at constant initial ozone concentration, was found to be proportional to cyanogen concentration.

The appearance of the 2205-cm^{-1} band could be quenched by the addition of Ar, SF_6, or N_2; N_2 was a much more effective quencher than either Ar or SF_6, which had about equal quenching efficiencies. When the reaction was quenched with N_2, N_2O was formed as a stable product. A new, weak absorption appeared at 2282 cm^{-1} when a mixture of 1.3 Torr O_3, 4.6 Torr C_2N_2, and 195 Torr N_2 was repetitively flashed. (Under these conditions the 2205-cm^{-1} band was completely quenched.) After ten flashes the O_3 had completely disappeared and no further changes were noted in the spectrum.

When the photolytic radiation was filtered through 4 mm of Pyrex, the 2205-cm^{-1} band did not appear. Instead, weak absorptions were observed at 2282 ± 10 and 2252 ± 10 cm^{-1}; the intensity of these bands could be increased by repeated flashing of the same sample. Thus the filtered flash and N_2-quenched experiments produced the same species, absorbing at 2282 cm^{-1}. The 2252-cm^{-1} species could not be observed in the N_2-quenched experiments, since this frequency overlaps the region of N_2O absorption.

The spectral region between 900 and 2500 cm^{-1} was studied and no other bands (apart from those of C_2N_2, O_3, N_2O) were observed.

Discussion

The flash photolysis of pure ozone initiates a chain decomposition in which virtually all the ozone is converted to oxygen. McGrath and Norrish[11,12] have given evidence for the energy chain mechanism

$$O_3 \xrightarrow{h\nu} O_2 + O \qquad (IV)$$

$$O + O_3 \longrightarrow O_2^\dagger(X^3\Sigma_g^-, v = 12\text{–}16) + O_2 \qquad (V)$$

$$O_2^\dagger + O_3 \longrightarrow 2O_2 + O \qquad (VI)$$

Their results clearly demonstrate that the electronic state of the atomic chain carrier is ^1D.

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(5) N. Basco, *Proc. Roy. Soc., Ser. A*, **283**, 302 (1965).

(6) T. Morrow and W. D. McGrath, *Trans. Faraday Soc.*, **62**, 642 (1966).

(7) C. W. Hand, R. M. Hexter, and P. Z. Kaufmann, *Appl. Opt.*, **5**, 1097 (1966).

(8) R. M. Hexter and C. W. Hand, *ibid.*, **7**, 2161 (1968).

(9) "Ozone Chemistry and Technology," Advances in Chemistry Series, No. 21, American Chemical Society, Washington, D. C., 1959, p 43.

(10) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand, Co., Princeton, N. J., 1967.

(11) W. D. McGrath and R. G. W. Norrish, *Proc. Roy. Soc., Ser. A*, **242**, 265 (1957).

(12) W. D. McGrath and R. G. W. Norrish, *Nature*, **186** 235 (1958).

At wavelengths shorter than 3000 Å, the primary process (IV) produces exclusively O(^{1}D) rather than the ground state O(^{3}P).[13] Flash photolysis radiation extends both above and below 3000 Å, but inasmuch as the extinction coefficient for ozone is comparatively small above 3000 Å,[14] we expect that the flash photolysis of ozone will result primarily in O(^{1}D). In contrast, if the flash radiation is filtered through Pyrex the photolysis product will be primarily O(^{3}P).

It is probably inappropriate to regard the flash photolysis of C_2N_2–O_3 mixtures as initiating the combustion of cyanogen; rather, cyanogen should be viewed as an additive which quenches the decomposition of ozone. This is very definitely chemical quenching rather than physical, inasmuch as the cyanogen–ozone mixtures are explosive.

From reactions V and VI we see that there are two possible quenching reactions

$$C_2N_2 + O \longrightarrow \text{product} \qquad \text{(VII)}$$

$$C_2N_2 + O_2^{\dagger} \longrightarrow \text{product} \qquad \text{(VIII)}$$

and a choice between them can be made by considering the effect of added inert diluent on the reaction. If the vibrationally excited oxygen molecule is the important species, SF_6 ought to be a very efficient competitor in reaction VIII, much better, certainly, than Ar or N_2. The results show, however, that SF_6 is no better than Ar and considerably less effective than N_2 in suppressing the appearance of the 2205-cm^{-1} band. Thus, reaction VII must be the important one. Furthermore, it is known that the two-body reaction

$$N_2 + O(^1D) \longrightarrow N_2 + O(^3P) \qquad \text{(IX)}$$

is a moderately efficient means of deactivating excited oxygen atoms.[15,16] The N_2O which appears in the N_2 quenched experiments is probably formed in the three-body reaction

$$N_2 + O + M \longrightarrow N_2O + M \qquad \text{(X)}$$

which can be expected to occur with either O(^{3}P) or O(^{1}D). Thus it appears that the species giving rise to the absorption at 2205 cm^{-1} is the product of reaction VIIa, most likely C_2N_2O.

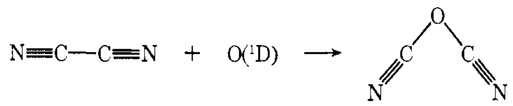
$$C_2N_2 + O(^1D) \longrightarrow C_2N_2O \qquad \text{(VIIa)}$$

The extent of reaction is much less when the photolyzing radiation is filtered through Pyrex. Many flashes are required to consume all the ozone, whereas with the unfiltered radiation most of the ozone disappears on a single flash. It is clear that, under our conditions of pressure and composition, filtering the flash effectively prevents the chain decomposition by reactions V and VI. What remains is the primary step, reaction IV, with the oxygen atom being produced in its ground state ^{3}P; the absorption bands which appear at 2282 and 2252 cm^{-1} must be attributed to the product of the reaction

$$C_2N_2 + O(^3P) \longrightarrow C_2N_2O \qquad \text{(VIIb)}$$

Evidence supporting this conclusion is provided by the results of the unfiltered flash experiments with added nitrogen. At high nitrogen pressures the chain decomposition of ozone is suppressed, and furthermore, most of the O(^{1}D) produced in the primary act will be deactivated by reaction IX. Thus, under these circumstances, the reaction VIIb should also be important, and we expect, and find, that the results are similar to those of the filtered flash experiments. That is, the 2282-cm^{-1} band is observed in both cases; the 2252-cm^{-1} band is not observed in the nitrogen-quenched experiments, but cannot be said to be absent since it could be obscured by the N_2O absorption. The N_2O is formed by reaction X and is of course not present to any great extent in the filtered flash experiments.

It remains now to discuss the possible structures of the products of reactions VIIa and VIIb. It is generally accepted in the chemistry of methylene that triplet CH_2 does not undergo insertion reactions into single bonds, whereas singlet CH_2 does so with ease.[17] We can therefore argue, by analogy with CH_2, that the isoelectronic O^{3}P cannot undergo insertion reactions and that O(^{1}D) can. Thus



(VIIa)

The insertion product is identified with the 2205-cm^{-1} absorption band, and the 2282-cm^{-1} and 2252-cm^{-1} bands are identified with an addition product, whose structure is not so well defined. Several possibilities suggest themselves, but none is an outstanding candidate. It is probably better to designate the addition product simply as C_2N_2O, remembering that it is distinct from the addition product NCOCN.

There are several experimental findings in the literature which bear on these product identifications. O(^{1}D) has been shown to undergo insertion reactions with propane[18] and methane,[19] yielding propanol and methanol. In the methane study it was demonstrated that the corresponding insertion of O(^{3}P) occurs to only a negligible extent if at all.

Since the species NCO is known, and indeed is produced in the flash photolysis of C_2N_2–O_3 mixtures,[6] it might be argued that we have observed this species. However, NCO is highly reactive[20] and therefore the continued existence, on a time scale of several minutes, of the transient species in our experiments argues against their identification with NCO. Furthermore, NCO has been positively identified in matrix isolation experiments[21] and its three fundamental vibration frequencies are 487, 1275, and 1922 cm^{-1}. There is little possibility that our observations may be correlated with these.

The assignment of the 2205-cm^{-1} band to NCOCN is suggested also by analogy to the known absorption

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(13) W. B. DeMore and O. F. Raper, *J. Chem. Phys.*, **44**, 1780 (1966).

(14) E. C. Y. Inn and Y. Tanaka, *J. Opt. Soc. Amer.*, **43**, 870 (1953).

(15) K. F. Preston and R. J. Cvetanović, *J. Chem. Phys.*, **45**, 2888 (1966).

(16) W. DeMore and O. F. Raper, *ibid.*, **37**, 2048 (1962).

(17) J. A. Bell, "Progress in Physical Organic Chemistry," Vol. 2, S. G. Cohen, A. Streitwieser, and R. W. Taft, Ed., Interscience Publishers, New York, N. Y., 1964.

(18) H. Yamazaki and R. J. Cvetanović, *J. Chem. Phys.*, **41**, 3703 (1964).

(19) W. B. DeMore and O. F. Raper, *ibid.*, **46**, 2500 (1967).

(20) R. N. Dixon, *Phil. Trans. Roy. Soc. London, Ser. A*, **252**, 165 (1960).

(21) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **47**, 5157 (1967).

bands of NCSCN and NCSeCN. The antisymmetric $C\equiv N$ stretching frequencies in these analogs are 2179 cm^{-1} in NCSCN;[22] and 2178 cm^{-1} in NCSeCN.[23]

Acknowledgment. We are grateful to the Air Force Office of Scientifie Research for financial support.

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(22) D. A. Long and D. Steele, *Spectrochim. Acta*, **19**, 1731 (1963).

(23) E. E. Aynsley, N. N. Greenwood, and M. J. Sprague, *J. Chem. Soc.*, 704 (1964).

On the Correlation between Structure and Dipole Moments in the Excited States of Substituted Benzenes[1]

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Abstract: The results of several recent high resolution spectroscopic investigations which measure dipole moments and structural parameters in the first excited $\pi^* \leftarrow \pi$ states of several substituted benzenes (phenol, aniline, *p*-fluorophenol, and *p*-fluoroaniline) are examined. The observed correlation between structure and moment allows us to make some definite observations as to the nature of intramolecular charge transfer on excitation, and this in turn allows a careful examination of various theoretical models for electronic structure in excited states.

Recent advances in the technology of high resolution optical spectroscopy coupled with increasing availability of computational techniques for spectral analysis have made possible determination of properties of molecules in excited electronic states to a high degree of accuracy. Spectral studies of polyatomic molecules in the gas phase under increasing resolution have revealed in numerous cases spectra rich in fine structure arising from transitions between individual rotational levels of the ground state to corresponding levels in the excited electronic state.[2] Just as the rotational energy levels deduced from microwave spectroscopy provide detailed and accurate information concerning molecular moments of inertia (and thereby bond lengths and bond angles) in the ground states, studies of the rotational fine structure of electronic spectra lead to accurate structural parameters of molecules in excited electronic states. Even for rather large molecules (*i.e.*, naphthalene, indole), though the spectra are complex, computers have enabled rotational analyses to be carried out.

The application of an external electric field (Stark effect) to polar molecules in the gas phase removes the spatial degeneracy (since all directions in space are no longer energetically equivalent) resulting in a splitting of observed rotational lines. This splitting is proportional to the difference in dipole moment between the two electronic states, and its measure allows accurate determination of dipole moments in excited electronic states.[3] The dipole moment is a sensitive measure of the electron density and consequently has been of inestimable value in understanding chemical properties of molecules in ground electronic states. It is thus expected that such measurements will be similarly helpful in understanding the nature of excited states.

From a chemical standpoint the actual values of various measured parameters sometimes are not as valuable as their relation to each other or their comparative values in a series of chemically related compounds. Such correlations are often quite valuable in understanding substituent effects, trends in reactivity or stability, and numerous other important properties, not to mention their predictive value.

An additional by-product of the computer age is the increasing availability of calculated wave functions for molecules in both ground and excited states. It is therefore also valuable to examine their relative ability to provide accurate predictive information concerning molecular properties.

It is the purpose of this paper to bring together results of several measurements of excited state structural parameters and dipole moments in a series of substituted benzenes. The observed correlation between structure and moment allows us to make some definite observations as to the nature of intramolecular charge transfer on excitation, and this in turn allows a careful examination of various theoretical models for electronic structure in excited states.

Experimental Results and Their Relationships

Rotational analyses of the lowest lying singlet $\pi^* \leftarrow \pi$ transitions ($B_2 \leftarrow A_1$) of aniline, phenol, *p*-fluoroaniline, and *p*-fluorophenol have recently been carried out by Christoffersen, Hollas, and Kirby.[4] The 0–0 vibrational bands were analyzed in each case. The resulting changes in rotational constants are listed in Table I. Although it is impossible to extract specific bond lengths and angles from rotational constants without extensive isotopic studies, it is possible to make some

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(1) Supported by NSF Grant No. GP 11530.

(2) J. M. Hollas, *Spectrochim. Acta*, **22**, 81 (1964); K. K. Innes and J. E. Parkin, *J. Mol. Spectrosc.*, **21**, 66 (1965); J. R. Lombardi, W. Klemperer, H. Basch, M. Robin, and N. A. Kuebler, *J. Chem. Phys.*, **51**, 33 (1969); A. Mani and J. R. Lombardi, *J. Mol. Spectrosc.*, **31**, 308 (1969).

(3) D. E. Freeman and W. Klemperer, *J. Chem. Phys.*, **40**, 604 (1964); **45**, 52 (1966); D. E. Freeman, J. R. Lombardi, and W. Klemperer, *ibid.*, **45**, 58 (1966); J. R. Lombardi, D. Campbell, and W. Klemperer, *ibid.*, **46**, 3482 (1967); J. R. Lombardi, D. E. Freeman, and W. Klemperer, *ibid.*, **46**, 2746 (1967); J. R. Lombardi, *ibid.*, **48**, 348 (1968).

(4) (a) J. Christoffersen, J. M. Hollas, and G. H. Kirby, *Proc. Roy. Soc., Ser. A*, 307, 97 (1968); (b) *Mol. Phys.*, inpress; (c) manuscript in preparation.