Reactions of ¹D and ³P Oxygen Atoms with Cyanogen by Flash Photolysis

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The reactions of ground-state and first-excited-state oxygen atoms with cyanogen have been investigated using the technique of flash photolysis and kinetic spectroscopy. In experiments using ozone+cyanogen mixtures under conditions where only the ozone is decomposed by the photolytic flash to give O^1D , it was possible to detect absorption due to CN and NCO together with other transient spectra in the regions 2807, 3290, 3920 and 4265 Å. From the kinetic evidence described in this work together with spectroscopic data obtained elsewhere these latter spectra would appear to be due to the free NCN radical. No transient species were observed during the photolysis of nitrogen dioxide+cyanogen mixtures where the reaction involved is that between ground-state (^{3}P) oxygen atoms and cyanogen. Investigations were also carried out on cyanogen was dissociated to a considerable extent and reactions between free CN radicals and molecular oxygen were studied.

From the results obtained it is concluded that ground-state oxygen atoms do not react with cyanogen to any appreciable extent at room temperature, whereas O^1D atoms react rapidly,

$$O^1D + C_2N_2 \rightarrow NCO + CN.$$

The reaction between free CN radicals and molecular oxygen is also fast, again leading to the formation of NCO according to

$$CN+O_2 \rightarrow NCO+O(^3P).$$

Subsequent reactions leading to the production of NCN radicals are discussed.

Extensive thermochemical ¹ and kinetic ² studies have been carried out on cyanogen flames and many reactions involving free CN radicals have been postulated to occur during the combustion of cyanogen and hydrocarbons in air,³⁻⁶ and in active nitrogen flames.⁷⁻⁹ There is, however, little reliable data available on the elementary processes involved, and in particular on the differences in behaviour between ground-state and excited oxygen atoms in their reactions with cyanogen. Using flash photolytic techniques it is possible to distinguish between these reactions by using nitrogen dioxide and ozone as sources for $O(^{3}P)$ and $O(^{1}D)$ respectively, since cyanogen itself absorbs at such short wavelengths that it is possible to ensure primary dissociation of the atomic oxygen sources only. The elementary reactions of the free CN radical itself can also be studied using the concentric spectrosil reaction vessel and flash tube arrangement, described previously,¹⁰ which is capable of photolyzing an appreciable amount of the cyanogen.

EXPERIMENTAL

APPARATUS

The apparatus and experimental technique have been described elsewhere.^{11, 12} The conventional flash tube and reaction vessel assembly initially used, consisting of a quartz

reaction vessel and flash tube lying side by side in a magnesium-oxide-coated reflector, did not result in any detectable production of CN radicals from cyanogen, when fired at 1280 J. This was undoubtedly due to the weak absorption characteristics of cyanogen within the transmission limits of the quartz,^{13, 14} and so the conventional set-up was used to study reacting systems in which it was not desirable to dissociate the cyanogen directly in the photolytic flash.

In order to obtain a reasonable percentage dissociation of the cyanogen on flashing it was necessary to modify the apparatus so that a higher output of light was obtained in the shorter wavelength region, where the cyanogen absorption is reasonably strong. This was accomplished by combining the flash tube and reaction vessel in a condenser-like arrangement (fig. 1) in which the photolytic flash occurred in the annular space D surrounding the inner reaction vessel C which was made of spectrosil. The end windows B of the reaction vessel were also of spectrosil and the electrodes E and F were identical to those already described.¹² In order to concentrate as much light as possible into the reaction vessel the outer flash tube similar to that described above was also made of Pyrex glass in order to study the reactions of $O(^{3}P)$ with cyanogen, using nitrogen dioxide as the atomic oxygen source.



FIG. 1.—Flash tube and reaction vessel assembly.

A, gas inlet to reaction vessel; B, quartz end windows; C, reaction vessel; D, photolytic flash tube; E, electrode and gas inlet; F, electrode

Flash energies of 1280 J were used in all experiments and absorption spectra were taken using a Lyman discharge tube spectroscopic flash,¹¹ triggered at pre-set delay times after firing of the photolytic flash. Spectra were taken using a quartz Littrow spectrograph (Hilger B478), recorded on Ilford Selochrome or Ilford Q plates, and developed using a high contrast developer (D19b).

PREPARATION AND PURIFICATION OF GASES

CYANOGEN.—Dry silver cyanide was heated under vacuum and the resulting cyanogen frozen out using liquid nitrogen. The product was degassed and purified by trap-to-trap distillation.

OZONE.—Well-dried cylinder oxygen was passed through four Siemens ozonizers joined in series at a rate of about 200 ml/min. A solution of copper sulphate acted as current carrier for the ozonizer and the power was supplied from a 10,000 V 50 c/sec transformer. The ozonized oxygen was condensed in a trap cooled with liquid nitrogen and the liquid oxygen which condensed was pumped off using the rotary pump. The residual ozone was then purified by bulb-to-bulb distillations.

NITROGEN DIOXIDE.—This was prepared by heating lead nitrate in a stream of air. The resulting gas was dried by passing it over phosphorous pentoxide and condensed in a trap cooled with an acetone+solid CO_2 mixture. It was then purified by trap-to-trap distillation under vacuum.

ARGON, NITROGEN, NITROUS OXIDE AND OXYGEN (B.O.C. cylinders) were used without further purification.

RESULTS

REACTIONS OF O^1D with cyanogen

Cyanogen+ozone mixtures (ratio 1:1) were flash photolyzed under isothermal conditions (i.e., with 10-50-fold excess of inert gas present) using 3 mm Hg partial pressure of cyanogen. Spectra obtained at short delay times after flashing the above mixtures in the conventional type reaction vessel show strong absorption due to excited oxygen molecules with v'' up to 17 and CN radicals with v'' up to 4. In addition, the absorption spectra of two other transient species were observed. The first of these species was the NCO radical. Both systems of NCO appeared strongly, i.e., $B(2\Pi_i) - X(2\Pi_i)$ at 2620 Å and $A(2\Sigma^+) - X(2\Pi_i)$ at 3600 Å. Detailed analyses on both these systems have been carried out by Dixon.^{15, 16}

The absorption spectrum of the second species consisted of a series of complex bands in the wavelength region 3250-3330 Å; this has been attributed to the free fulminate (C—N—O) radical.¹⁰ A detailed rotational analysis of this system has, however, been carried out by Herzberg and Travis ^{17, 18} who attribute the spectrum to the CN₂ radical.

The absorption spectra due to excited oxygen, NCO, CN and CN₂ all appear strongly at 15 m sec, but whereas the excited oxygen decays rapidly and has completely disappeared at 50 μ sec, the CN₂ and CN intensities decay slowly to zero at 500 μ sec and 2.5 msec respectively. The NCO intensity, however, seems to follow a slightly different pattern being strong at 15 μ sec, weak at 50 μ sec, reappearing strongly at 500 μ sec and finally decaying to zero at 2.5 msec. The continuous absorption due to ozone has completely disappeared after 50 μ sec.

When a cyanogen + ozone mixture (ratio 5:1) with excess inert gas was flashed using the concentric spectrosil set-up, in order to decompose all the ozone rapidly so that the spectral region below 3000 Å could be studied at short delay times, only very weak excited oxygen absorption was observed even at the shortest delay used, i.e., 15 μ sec (see fig. 2). The absorption spectra of CN, CN₂ and NCO were, however, observed at all delay times from 15 μ sec to 2.5 msec. In addition to these systems, another three diffuse absorption bands degraded to the red with heads at 4265, 3920 and 2807 Å were also observed.

When a cyanogen + ozone + argon mixture of ratio 5:1:30 was flashed, a study of the spectral region 2200-2850 Å revealed the presence of a small quantity of excited NO molecules with v'' = 1 at the shortest delay time observable (i.e., $40 \ \mu$ sec). This excited NO absorption gradually decayed with time but weak (0,0) NO absorption was observable on the infinity shot.

REACTIONS OF $O^{3}P$ with cyanogen

Spectra obtained during the isothermal flash photolysis of a cyanogen + nitrogen dioxide mixture (ratio 5:1) using the concentric spectrosil reaction vessel showed the presence of the weak 2807 Å system, the CN₂ system and the CN $\Delta v = 0$ system (see fig. 3). The NCO, 4265 and 3920 Å bands observed with the ozone + cyanogen mixtures were not present but this may have been due to strong NO₂ absorption in these regions. The CN intensity increased to a maximum at 25 μ sec and then rapidly decayed to zero at 80 μ sec, whereas the CN₂ intensity, which was also at a maximum at 25 μ sec, decayed slowly to zero at 500 μ sec. When the same mixture (i.e., 5:1, C₂N₂/NO₂) was flash photolyzed isothermally using a concentric type reaction vessel made of Pyrex glass, no transient spectra or other signs of reaction were observed.







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3290





- NCN

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ABS

-SPECTROSIL-

¥ 1

-PYREX-

REACTIONS OF CN RADICALS WITH OXYGEN AND NITROUS OXIDE

Spectra obtained during the isothermal flash photolysis of a cyanogen+oxygen mixture (ratio 1:1) using the conventional reaction vessel showed only exceedingly weak NCO absorption. This was presumably due to the small amount of cyanogen decomposition obtained using the conventional apparatus. (When cyanogen+inert gas mixtures were flashed in this conventional apparatus no CN radical absorption could be detected.)

Adiabatic and isothermal flash photolysis of cyanogen using the concentric spectrosil reaction vessel and flash tube resulted in the production of an appreciable



FIG. 4.—Concentration of CN, NCO, NCN and X as a function of $P(O_2)$ at 50 µsec delay.

amount of CN radicals with v'' up to 4. However, spectra obtained during the adiabatic and isothermal flash photolysis of an oxygen+cyanogen mixture (ratio 1:1) showed no sign of CN absorption but both absorption systems of the NCO radical, along with the exceedingly weak 3250-3330 Å system due to CN₂, were observed. The intensities of the absorption bands due to CN₂ and NCO decreased with increasing delay time and had completely disappeared after 50 and 500 μ sec respectively.

A range of mixtures each containing 15 mm Hg partial pressure of cyanogen but varying amounts of oxygen were isothermally flash photolyzed using the same delay time, i.e., 50 μ sec, and the spectra obtained showed the same NCO, CN, CN₂ 2807, 3920 and 4265 Å systems obtained from ozone+cyanogen mixtures. The kinetic behaviour of the NCO, CN₂ CN and 4265 Å X systems with increasing oxygen concentration is shown in fig. 4. The radical concentrations, in arbitrary units, were obtained from photometric tracings of the spectra reported above. The 2807 and 3920 Å bands seemed on visual examination to follow a similar kinetic pattern to the 4265 Å band but they were too weak for an accurate photometric trace to be made. As may be seen from fig. 4, increase in the oxygen concentration resulted in suppression of the CN concentration at 50 μ sec but increased the NCO concentration up to a maximum after which it also decayed with further increase in the oxygen concentration. The CN₂ and 4265 Å absorber concentrations, however, had sharp maxima at about 0.1 mm Hg of oxygen. Increase of the oxygen pressure above this limit resulted in suppression of these bands.

When a $C_2N_2+O_2+argon$ mixture of composition 15 mm : 0·1 mm : 50 mm Hg was flash photolyzed, the CN₂, CN, 4265, 3920 and 2807 Å systems observed all seem to have maxima at about 25 μ sec and then gradually decay to zero at 2·5 msec whilxt the NCO system is at its maximum intensity at 15 μ sec and decays rapidly to zero at about 250 μ sec.

Spectra obtained during the isothermal flash photolysis of a cyanogen + oxygen mixture of ratio 1:5 using the concentric spectrosil set-up showed only the presence of strong NCO absorption and exceedingly weak CN₂ absorption both having their maxima at 7.5 μ sec and decaying rapidly to zero at 50 μ sec. Examination of the spectral region 2200-2850 Å showed the presence of NO with v'' = 0 (relatively strong) and v'' = 1 (weak) even at the shortest delay time used, i.e., 7.5 μ sec. Experiments carried out on the isothermal flash photolysis of C₂N₂+N₂O mixtures of varying composition using the concentric spectrosil reaction vessel showed only absorption due to the free CN radical indicating little or no reaction between CN and N₂O.

DISCUSSION

ASSIGNMENT OF SPECTRA

Controversy exists concerning the assignment of the four new absorption systems observed during this work, i.e., the 3250-3330, 2807, 3920 and 4265 Å bands. Previously,¹⁰ we assigned the 3250-3330 Å system to the free fulminate (C—N—O) radical. The principal argument is the necessary presence of oxygen in the reacting mixture before the 3250-3330 Å system may be obtained. Further support was obtained by flash photolyzing fulminic acid which also gave the same 3250-3330 Å bands together with an additional four complex band systems in the regions 3065-3100, 3165-3175, 3340-3380 and 3425-3450 Å which have not yet been identified.

Similar series of bands in the spectral region 3250-3330 Å to those reported above have been detected in emission from flames supported by active nitrogen by Jennings and Linnett⁸ and from cyanogen+oxygen chilled flames by Thomas, Gaydon and Brewer.¹ Jennings and Linnett attributed their bands to an emitter containing only carbon and nitrogen and so concluded that the most likely emitting species were C_2N , CN_2 or some excited state of cyanogen. Thomas, Gaydon and Brewer attributed their bands to the CNO radical, by analogy with HCO obtained in hydrocarbon chilled flames.

A more detailed analysis of the system has, however, been carried out by Herzberg and Travis,^{17, 18} and although these workers did not attempt any oxygen isotope experiments to show absence of oxygen in the absorbing species, they conclude from the spectroscopic data obtained that the 3250-3330 Å system is due to the $2\Pi_u$ (inv) $-3\Sigma^-$ transition of the linear symmetric molecule NCN. This conclusion is also supported by the work of Pontrelli and Anastassiou ¹⁹ who observed the 3250-3330 Å system during the flash photolysis of N₃CN.

The bands at 4265 and 3920 Å were also observed by Basco 20 and from their observed kinetics were attributed to either N₂C₂O or N₂C₂O produced by the reactions

$$CN + NCO \rightarrow N_2C_2O \tag{1}$$

 $CN + NCO_2 \rightarrow NCO_2 CN.$ (2)

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As seen from fig. 4 the kinetic behaviour of the CN_2 bands is similar to that of the 4265 Å X system observed by Basco and it is likely that both belong to the same absorber. Although the 3920 and 2807 Å systems were too weak for accurate photometric measurements to be made they would also seem from a visual examination, to follow the same behaviour.

It is therefore concluded that the four new absorption systems observed in these experiments belong to the one absorbing species and this species is the NCN radical. This conclusion is also in agreement with the kinetics and reaction mechanisms discussed below.

KINETICS AND REACTION MECHANISMS

REACTIONS OF O(1D) WITH CYANOGEN

When ozone + cyanogen mixtures are flash photolyzed in the conventional reaction vessel the amount of direct photolytic decomposition of the cyanogen is extremely small and the effect of the photolytic flash is therefore confined to the dissociation of the ozone. Ozone decomposes under these conditions as ²¹

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$$O_3 \rightarrow O_2 + O(^1D). \tag{3}$$

In the absence of competitive reactions for the removal of oxygen atoms, reaction (3) is followed by the fast reaction (4) resulting in the production of vibrationally excited oxygen molecules :

$$O(^{1}D) + O_{3} \rightarrow O_{2_{v}}^{*} + O_{2}.$$
 (4)

When the cyanogen and ozone were present in equimolar amounts in the cyanogen + ozone + argon mixtures used in these experiments, vibrationally-excited oxygen molecules with v'' up to 17 were produced by reaction (4) and easily detected at short delay times. When the cyanogen/ozone ratio was increased to 5:1 this spectrum due to excited oxygen molecules disappeared (fig. 2) indicating the preferential removal of O¹D by a reaction involving cyanogen molecules. The reaction of O¹D with cyanogen produces large concentrations of CN and NCO radicals, whose absorption spectra are observed to be at their maximum intensities at the shorter delay times, and must proceed as follows:

$$O(^{1}D) + N \equiv C - CN \rightarrow C \equiv N + NCO.$$
⁽⁵⁾

An estimate for the heat of reaction (5) cannot be given due to the lack of reliable thermochemical data for the NCO radical. Dixon ¹⁵ gives a value of 64 kcal/mole for the dissociation energy of NCO into N+CO and estimates the dissociation energy of the CO bond to be 0.6 eV greater than that of the CN bond. This would give a value of 78 kcal/mole for the dissociation energy of NCO into CN+O, but the uncertainty in both these values given by Dixon could be as high as ± 25 kcal. Taking D(NC-CN) as 145 kcal/mole, reaction (5) would be 21 kcal ± 25 kcal endothermic. From the observed strengths of the CN and NCO spectra obtained it is likely that reaction (5) would be fast and exothermic, indicating that D(N-CO)and D(NC-O) should be at least 89 kcal/mole and 103 kcal/mole respectively. These values are within the uncertainty limits of ± 25 kcal given by Dixon and would also be in better agreement with the value for D(O-CO) of 125 kcal/mole, obtained by taking D(C-O) as 381 kcal/mole.

If the new absorption spectra observed at 2807, 3250, 3920 and 4265 Å do belong to the NCN radical the most likely reaction for its production is (6).

$$CN + NCO \rightarrow NCN + CO.$$
 (6)

REACTIONS OF OXYGEN ATOMS WITH CYANOGEN

Reaction (6) would be exothermic by an amount equal to the difference between D(N-CN) and D(N-CO). This difference would probably be at least 20 kcal/ mole due to the lower stability of CN compared with CO. Reaction (6) would therefore be expected to be a fast reaction. This mechanism is also in agreement with the observed kinetics of fig. 2, where the NCN intensity reaches a maximum at the shorter delay times when large concentrations of CN and NCO are present in the reaction mixture, and the intensity of the NCN decays as the CN and NCO concentrations fall.

All or some of the 2807, 3920 and 4265 Å bands could, however, be due to a species of structure NCNCO formed by the reaction

$$CN + NCO \rightarrow NCNCO,$$
 (7)

provided this NCNCO species then decomposed rapidly giving NCN and CO, according to (8),

$$NCNCO \rightarrow NCN + CO. \tag{8}$$

It therefore remains only to explain the presence of the small amounts of vibrationally excited nitric oxide in the reaction mixtures at the shorter delay times. The most probable mechanisms for the production of vibrationally excited nitric oxide here would undoubtedly be

$$O(^{1}D) + NCO \rightarrow NO_{v}^{*} + CO$$
⁽⁹⁾

$$O(^{1}D) + NCN \rightarrow NO_{v}^{*} + CN.$$
⁽¹⁰⁾

These reactions are of the type known to produce vibrationally excited species ²² and sufficient energy would undoubtedly be present for their production.

The reaction

$$O(^{1}D) + C_{2}N_{2} \rightarrow NO + C_{2}N \tag{11}$$

would also be about 20 kcal exothermic, taking $D(NCC \equiv N) = D(CN) = 175$ kcal/ mole and D(NO) as 150/mole, and so could result in the production of vibrationally excited NO molecules. However, since no spectra which could be attributed to the C₂N radical were observed during any of these experiments, reaction (11) would not seem to occur to any appreciable extent.

Although the reaction

$$CN + O_2 \rightarrow NO + CO$$
 (12)

is over 100 kcal/mole exothermic it is not of the type known to produce vibrationallyexcited products.

REACTIONS OF $O(^{3}P)$ WITH CYANOGEN

When cyanogen+nitrogen dioxide+argon mixtures were flashed in the spectrosil concentric reaction vessel the results obtained were identical to those obtained with cyanogen+ozone+argon mixtures and it was at first thought that there was little difference in reactivity between $O(^{1}D)$ and $O(^{3}P)$ with cyanogen. However, when the same mixture was flash photolyzed using a Pyrex concentric reaction vessel no indication of reaction between $O(^{3}P)$ and cyanogen was obtained (see fig. 3).

The processes occurring in the spectrosil concentric reaction vessel could be due to one or more of the following reactions :

$$CN + NO_2 \rightarrow NCO + NO$$
 (13)

$$CN + O_2 \rightarrow NCO + O$$
 (14)

$$O(^{1}D) + C_{2}N_{2} \rightarrow NCO + CN.$$
(15)

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Evidence for the photolytic production of $O(^1D)$ from NO₂ using the concentric spectrosil reaction vessel has already been found in this laboratory, and can be attributed to the increased output of light in the shorter wavelength region obtained using this type of reaction vessel. It would therefore seem that reaction (5) is the principal primary reaction operative when nitrogen dioxide+cyanogen+argon mixtures are flashed under these conditions, but reactions (13) and (14) will undoubtedly occur to some extent.

It is therefore concluded that $O(^{3}P)$, unlike $O(^{1}D)$, is not capable of reacting appreciably with cyanogen according to (15),

$$O(^{3}P) + C_{2}N_{2} \rightarrow NCO + CN.$$
(15)

The difference in reactivity of $O({}^{3}P)$ and $O({}^{1}D)$ with cyanogen is probably mainly due to a high activation energy for reaction (15). However, other factors, particularly the difference in spin between $O({}^{3}P)$ and $O({}^{1}D)$, may also play important roles.

REACTIONS OF CN FREE RADICALS WITH OXYGEN

The primary act following the absorption of radiation by cyanogen is dissociation into CN radicals. When oxygen is present in the reaction mixture the transient spectra of CN_2 and NCO are observed. The CN_2 arises from a reaction involving both CN and NCO radicals since it is observed (fig. 4) that the intensities of all four CN_2 bands obtained from a given pressure of cyanogen at a given delay time at first increase with the partial pressure of oxygen, reach a maximum and then decrease as the oxygen pressure is further increased. The effect of oxygen on the concentrations of CN and NCO over this pressure range is to decrease continuously the former to zero and increase the latter to a maximum. The CN_2 bands are only observed to be strong in the presence of appreciable concentrations of both CN and NCO indicating that the reaction mechanism is as follows :

$$CN + O_2 \rightarrow NCO + O \tag{14}$$

$$CN + NCO \rightarrow NCN + CO.$$
 (6)

Taking the bond strengths of CO, O_2 and CN to be 256, 118 and 175 kcal/mole respectively, reaction (14) is 27 kcal/mole exothermic if the dissociation energy of NCO into N+CO be taken as 64 kcal/mole. The uncertainty, however, in this value of the dissociation energy may be as high as ± 25 kcal/mole. It is therefore likely that the oxygen atom produced in (14) would be in the ground state, i.e.,

$$CN(^{2}\Sigma) + O_{2}(^{3}\Sigma_{g}^{-}) \rightarrow NCO(^{2}\Pi_{i}) + O(^{3}P)$$
(16)

This would also result in the conservation of total spin.

The NCO and NCN radicals could then polymerize, disproportionate or further react with oxygen as follows :

$$2NCN \rightarrow (NCN)_2 \tag{17}$$

$$2NCO \rightarrow (NCO)_2 \tag{18}$$

$$2NCN \rightarrow N_2 + C_2 N_2 \tag{19}$$

$$2NCO \rightarrow N_2 + 2CO \tag{20}$$

$$NCN + O_2 \rightarrow NO + CN + O \text{ or } NO + NCO$$
 (21)

$$NCO + O_2 \rightarrow NO + CO + O \text{ or } NO + CO_2$$
 (22)

$$NCN + NCO \rightarrow N_2 + CN + CO.$$
 (23)

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REACTIONS OF OXYGEN ATOMS WITH CYANOGEN

Mass spectrum analysis of the final products from the flash photolysis of cyanogen + oxygen + argon mixtures showed the presence of a small concentration of a stable product of mass 80, which would correspond with (NCN)₂, along with the expected mass number of 28 corresponding to CO and N₂.

The foregoing conclusions can therefore be summarized in the following scheme :

$$O(^{1}D) + C_{2}N_{2} \rightarrow NCO + CN$$
(5)

$$O(^{3}P) + C_2N_2 \rightarrow no$$
 appreciable reaction

$$CN + O_2 \rightarrow NCO + O(^{3}P) \tag{16}$$

$$CN + O_3 \rightarrow NCO + O_2 \tag{25}$$

$$NCO + CN \rightarrow NCN + CO$$
 (6)

$$2NCN \rightarrow (NCN)_2 \rightarrow N_2 + C_2N_2$$
 (17) and (19)

$$2NCO \rightarrow (NCO)_2 \rightarrow N_2 + 2CO$$
 (18) and (20)

$$O(^{1}D \text{ or } ^{3}P) + NCN \rightarrow NO_{v}^{*} + CN$$
 (26)

 $O(^{1}D \text{ or } ^{3}P) + NCO \rightarrow NO_{p}^{*} + CO$ (27)

COMBUSTION OF CYANOGEN

Many of the reactions discussed above will occur in cyanogen flames. Under high-temperature flame conditions the polymeric compounds produced in reactions (17) and (18) would undergo thermal decomposition as follows:

$$(NCN)_2 \rightarrow N_2 + 2CN \tag{26}$$

$$(NCO)_2 \rightarrow N_2 + 2CO, \tag{27}$$

and NO could probably react with CN as in (28).

$$NO + CN \rightarrow N_2 + CO. \tag{28}$$

The CO produced would then undergo further combustion to CO_2 with the result that the only reaction products obtained would be CO_2 , CO and N_2 . The high temperatures obtained using cyanogen+oxygen and cyanogen+ozone flames are undoubtedly due to the high rate constants of reactions involving cyanogen and CN radicals and the high stabilities of the reaction products. However, because of the high temperatures prevailing in cyanogen flames, many other reactions, some involving ionic species, not observed during these isothermal flash photolysis experiments will also have reasonably high rate constants.

- ⁶ Sugden and Rentzepis, Nature, 1964, 202, 448.
- ⁷ Brown and Broida, J. Chem. Physics, 1964, 41, 2053.
- ⁸ Jennings and Linnett, Trans. Faraday Soc., 1960, 56, 1737.
- ⁹ Setser and Thrush, Nature, 1963, 200, 864.
- ¹⁰ McGrath and Morrow, Nature, 1964, 203, 619.
- ¹¹ McGrath and McGarvey, Proc. Roy. Soc. A, 1964, 278, 490.
- ¹² McGrath and McGarvey, Trans. Faraday Soc., 1964, 60, 2196.
- ¹³ Pearse and Gaydon, *The Identification of Molecular Spectra* (Chapman and Hall Ltd., London, 1950), 2nd ed.

¹ Thomas, Gaydon and Brewer, J. Chem. Physics, 1952, 20, 369.

² Scheller and McKnight, 7th Int. Symp. Combustion, 1955, p. 55.

³ Norrish, Porter and Thrush, Proc. Roy. Soc. A, 1953, 216, 181.

⁴ Gaydon, The Spectroscopy of Flames (Chapman and Hall Ltd., London, 1957).

⁵ Cusin and James, J. Chim. Physique, 1961, 58, 162, 730.

- 14 Price and Walsh, Trans. Faraday Soc., 1945, 41, 386.
- 15 Dixon, Phil. Trans. A, 1960, 252, 165.
- 16 Dixon, Can. J. Physics, 1960, 38, 10.
- 17 Herzberg and Travis, Can. J. Physics, 1964, 42, 1658.
- 18 Herzberg, Travis, Morrow and McGrath, Nature, 1964, 204, 988.
- ¹⁹ Pontrelli and Anastassiou, J. Chem. Physics, 1965, 42, 3735.
 ²⁰ Basco, Proc. Roy. Soc. A, 1965, 283, 302.
 ²¹ McGrath and Norrish, Proc. Roy. Soc. A, 1957, 242, 265.
 ²² McGrath and Norrish, Z. physik. Chem., 1958, 15, 245.