DMSO-d_6 and in DMA.[31] In these experiments, no additional resonances could be observed and, hence, on the time scale necessitated by pmr techniques at 25° ($\sim$2.5 min),[1,15] the 1,3 complex of **5** is either not formed or is not detectable.

(31) DMA has been found to considerably enhance the stability of the 1,3-dimethoxy-2,4,6-trinitrocyclohexadienylide ion as compared to that in DMSO.[32] However, no 1,3-complex formation could be detected in the *in situ* formation of complex **1** from **6** either in DMSO-d_6[4] or in DMA.

(32) Unpublished work: J. W. Larsen, E. J. Fendler, and J. H. Fendler.

Electron Spin Resonance Studies of Radical Formation in Nucleophilic Addition Reactions. III. On the Mechanism of Radical Formation and Chemiluminescence in the Cyanide Addition and Oxygenation of N-Methylacridinium Chloride[1]

JOHN W. HAPP, EDWARD G. JANZEN,* AND BRUCE C. RUDY

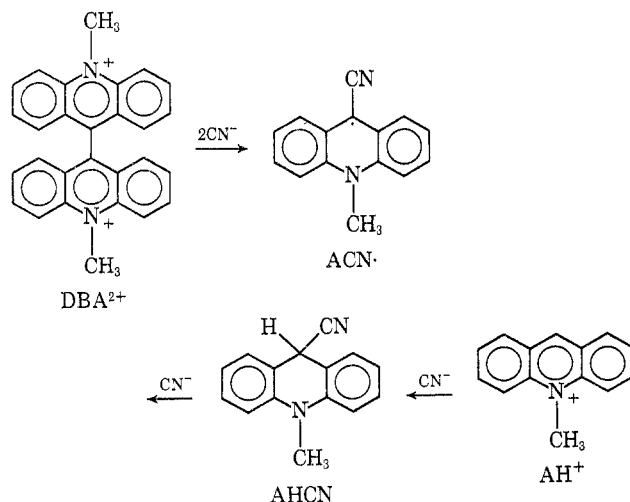*Department of Chemistry, The University of Georgia, Athens, Georgia 30601*

The reaction of KCN with N-methylacridinium chloride in 90% dimethyl sulfoxide–10% water produces N-methyl-9-cyanoacridan. With excess cyanide the red N-methyl-9-cyanoacridanide anion is produced. In the presence of oxygen N-methylacridone and potassium cyanate are produced with light emission. The reaction stoichiometry is shown to be
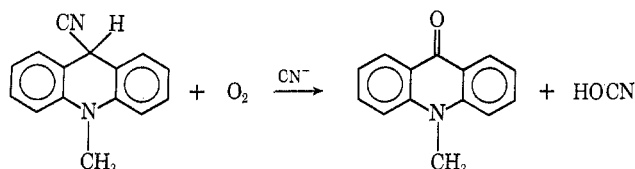
The initial rate of oxygen uptake shows the same dependence on the potassium cyanide concentration as the maximum light emission intensity on this variable and the time required to reach the light emission maximum is about the same as the time required for the major portion of the oxygen to be absorbed in the same experiment. The significance of these observations is discussed. In these experiments N-methyl-9-cyanoacridanyl is detected. A carbanion electron transfer oxidation mechanism involving this radical as an intermediate is suggested.

In a previous report[2] we described the detection of N-methyl-9-cyanoacridanyl radical in the cyanide ion addition to oxygen free solutions of lucigenin (N,N′-dimethyl-9,9′-biacridinium dinitrate) or to air-saturated solutions of N-methylacridinium chloride. The structure of the radical was verified by electrolytic reduction of N-methyl-9-cyanoacridinium chloride. The esr

* Author to whom correspondence should be addressed.
(1) This work was supported by the Atomic Energy Commission Contract No. AT-(40-L)-2851.
(2) Part II: J. W. Happ and E. G. Janzen, *J. Org. Chem.*, **35**, 96 (1970).

spectrum was analyzed and coupling constants assigned on the basis of molecular orbital calculations and by analogy to radicals of similar structure.

The unusual reaction between cyanide ion and N-methylacridinium chloride to produce N-methyl-9-cyanoacridanyl radicals (ACN$\cdot$)[3] in air-saturated solutions has been investigated in more detail. Reactions of N-methyl-9-cyanoacridan (AHCN) and the chemiluminescent production of N-methylacridone have also been studied.

Experimental Section

Equipment.—The esr and light detection equipment was the same as used for a previous study.[4] Relative chemiluminescence light emission was monitored using a Firefly photometer with a IP21 photomultiplier tube. Solutions of N-methylacridinium chloride were placed in the sample compartment of the photometer and an appropriate amount of potassium cyanide in the same solvent was injected by syringe into the solution so that the final volume of the reaction mixture was 5 ml. Oxygen was continuously bubbled through the reaction mixture and the intensity of chemiluminescence was recorded. Chemiluminescence spectra were obtained with an Aminco spectrophotofluorometer equipped with a xenon arc light and a IP28 photomultiplier tube. A typical solution contained 0.04 M N-methylacridinium chloride and 0.06 M potassium cyanide in 90% dimethyl sulfoxide –10% water (by volume) saturated with oxygen.

(3) For abbreviation,"A" is used as the symbol for the N-methylacridanyl moeity. "A" is followed by symbols representing the substituent(s) in the 9 position of the acridine ring.
(4) E. G. Janzen, J. B. Pickett, J. W. Happ, and W. DeAngelis, *J. Org. Chem.*, **35**, 88 (1970).

TABLE I

STOICHIOMETRY OF THE KCN ADDITION TO N-METHYLACRIDINIUM CHLORIDE[a]

AH[+]Cl^{-},[b] mmol	KCN, mmol	O_2,[c] mmol	Time, hr	Product[b]	Crude yield, mmol	Mp,[d] °C	CN^{-},[e] mmol
1.01	0.50	0.02	27	AHCN	0.50	136–138	Negative test
1.01	0.72		5.0	AHCN	0.68	115 (141–142[f])	Negative test
1.00	1.00	0.79	6.6	NMA	0.82	204.0–204.5	
1.00	1.51	0.74	2.1	NMA	0.80	199–200	0.63
1.00	1.52	0.93	40.1	NMA	0.88	203–204	Positive test
1.00	1.72	0.73	2.8	NMA	0.77	203.5–204.0	0.73
1.01	1.86		27	NMA	0.77	202–203	0.90

[a] Reaction run in 25 ml of 90% DMSO–10% water by volume and agitated by magnetic stirrer.   [b] AH[+] Cl^{-} = N-methylacridinium chloride, AHCN = N-methyl-9-cyanoacridan; NMA = N-methylacridone.   [c] Corrected to STP conditions.   [d] Lit. mp of AHCN 143°, NMA 204–205° uncorr.   [e] Determined by titration or by qualitative test described in text.   [f] After one recrystallization from absolute ethanol.

The rate and amount of oxygen absorption was monitored at constant (atmospheric) pressure and at room temperature using a volumetric gas absorption apparatus. The solution was vigorously shaken in a creased 200-ml flask by means of a wrist-action shaker constructed from a Waco stirrer. A typical flask is photographed, and the shaker diagrammed and the technique described in ref 5 and 6.

Chemicals.—The source of the chemicals needed in this study was reported previously.[2,4]

Isolation of Products.—The N-methyl-9-cyanoacridan produced in the reaction of potassium cyanide with N-methyl-9-cyanoacridinium chloride in 90% DMSO–10% H_2O was isolated by diluting the solution with water tenfold. The precipitate was filtered, washed with water, and dried under vacuum. Identification was by melting point (see Table I), nmr spectrum, color, and solubility in chloroform.
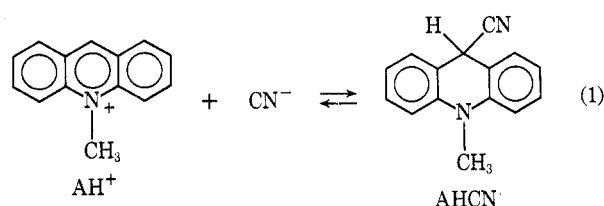
N-Methylacridone isolated from oxidation experiments with excess cyanide was obtained by diluting the solutions with tenfold excess of water and filtering. Identification was by melting point, mixture melting point with an authentic sample, nmr spectrum, color, and solubility.

Cyanide and Cyanate Determinations.—The solutions obtained from the oxidations were diluted with water and the N-methylacridone was filtered. Cyanide ion was determined in the filtrate with a standard solution of silver nitrate according to the Liebig–Deniges method.[7] No correction was made for the presence of 10% DMSO in the aqueous solution. Titration of standard aqueous KCN solutions indicated a 6% error at 0.002 M cyanide, 12% error at 0.001 M cyanide, and 31% error at 0.0005 M cyanide concentration due to the presence of the DMSO. Therefore, titrimetric analysis of cyanide ion was performed only on solutions of more than 0.002 M cyanide ion containing 10% DMSO.

The same filtrates were tested for cyanate ion by the addition of cobalt(II) chloride which forms a blue color in the presence of cyanate ion.[8] The test was negative for solutions of commonly used concentrations. Further experiments indicated that the limit of detection of KOCN in 10% DMSO–90% water by this method was 0.018 M KOCN. When N-methylacridinium chloride initially 0.5 M was oxidized in the presence of 0.7 M KCN, the filtrate at the end of the reaction after dilution to 90% water produced a blue color with $CoCl_2$. Appropriate control tests with and without KOCN verified that cyanide ion, methylacridone, and methylacridinium chloride did not interfere with the appropriate color formation.
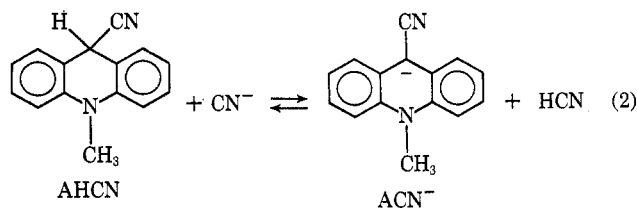
Results and Discussion

KCN Addition to N-Methylacridinium Chloride–N-Methyl-9-cyanoacridan.

—It is well known that the addition of cyanide ion to N-methylacridinium salts (AH[+]) yields AHCN.[9] In 90% dimethyl sulfoxide (DMSO) and 10% water (by volume), nearly quantita-

(5) E. G. Janzen, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1963.
(6) G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, *Advan. Chem. Ser.*, **51**, 112 (1965); see p 164–165.
(7) G. H. Ayres, "Quantitative Chemical Analysis," Harper and Bros., New York, N. Y., 1958, p 308.
(8) A. Scattergood, *Inorg. Syn.*, **2**, 86 (1946).
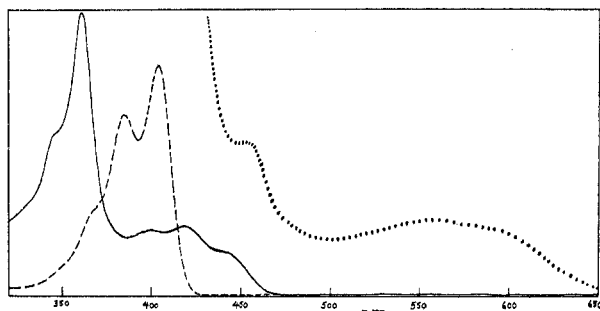(9) C. Kaufmann and A. Albertini, *Chem. Ber.*, **42**, 1999 (1909).

tive yields of AHCN could be isolated when potassium cyanide was added to excess N-methylacridinium chloride (see runs 1 and 2, Table I). Under such conditions in air-saturated solutions of AHCN in DMSO, dimethylformamide, benzene, or dimethoxyethane small concentrations of the ACN · radical could be detected, the polar solvents providing the highest concentration of radicals. In the crystalline solid state, AHCN was found to give an esr signal which in solution was due to ACN· radicals. The radical impurity was estimated to be approximately 1% and was enhanced by recrystallization in boiling absolute ethanol and removed by dissolving in chloroform. (The latter is probably the result of a reaction with solvent which produces N-methyl-9-cyanoacridinium chloride). Although the presence of small amounts of ACN· radicals in polar solvents appeared to be the result of air oxidation of AHCN, negligible amounts of oxygen were absorbed by AHCN solutions over long periods of time in experiments where oxygen uptake was monitored with a volumetric gas absorption apparatus.

Oxygenation of N-Methyl-9-cyanoacridanide Anion. —In the presence of potassium cyanide or potassium *tert*-butoxide, solutions of AHCN in DMSO acquire a cherry red color. These solutions give a broad absorption at 530–600 mμ (Figure 1). Since diphenylacetonitrile and 9-phenylfluorene also give colored solutions with KCN in DMSO which are typical of the carbanions (red and yellow-orange respectively), the cherry red color in the case of AHCN is attributed to formation of the carbanion (ACN[-]). The same coloration is

$$\text{AH}^+ + \text{CN}^- \rightleftharpoons \text{AHCN} \quad (1)$$

$$\text{AHCN} + \text{CN}^- \rightleftharpoons \text{ACN}^- + \text{HCN} \quad (2)$$

observed when *excess* cyanide is added to AH[+] solutions. The conclusion is that the *in situ* formation of AHCN (eq 1) is rapidly followed by carbanion formation (eq 2).

Figure 1.—Absorption spectra of *N*-methylacridinium chloride (——), *N*-methylacridone (- - - -), and *N*-methylacridinium chloride in the presence of excess KCN (······) in 90% DMSO–10% water. The *N*-methylacridinium chloride concentration in the latter was *ca.* three times the concentration in the former.
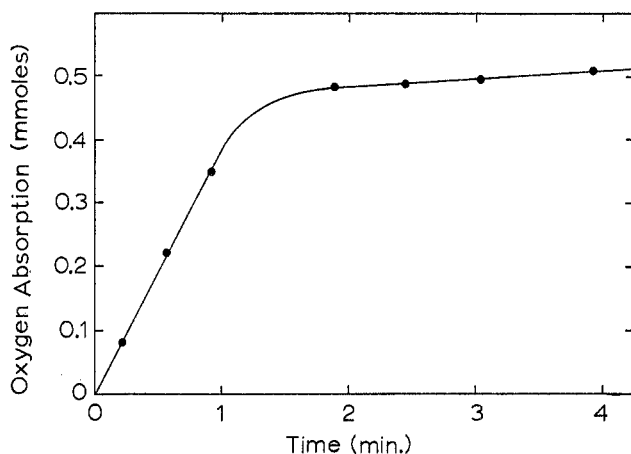

Figure 2.—Oxygen absorption as a function of time for 1.00 mmol of *N*-methylacridinium chloride and 1.52 mmol of potassium cyanide in 25 ml of 90% DMSO–10% water at 25.0°.

Solutions of ACN⁻ produced by the addition of excess cyanide to AH⁺ rapidly absorb oxygen. The plot of oxygen absorption *vs.* time is nonautocatalytic, *i.e.*, not S-shaped (Figure 2) and is typical of carbanionic oxidations.[5,6,10] The major portion (>50%) of the oxidation is over in 1–2 min. This portion of the plot is practically linear. Further absorption of oxygen gives a stoichiometry of 0.7–0.8 by 2–3 hr. The highest stoichiometry obtained was 0.93 after 40 hr (see Table I). These observations suggest a 1 to 1 stoichiometry between the moles of oxygen absorbed to the moles AH⁺ converted to NMA.

The *initial* slope of the oxygen absorption *vs.* time plot should depend on the initial concentrations of the reactants involved in the slow step. If the initial

$$[dO_2/dt]_{t=0} \propto [O_2]_0^m[AH^+]_0^n[CN^-]_0^p$$

concentration of AH⁺ is held constant and the exposure to oxygen is arranged to be the same in a series of runs where the concentration of cyanide ion is varied one might expect to obtain the order in cyanide ion for the oxygen absorption reaction. Such data has been obtained (Table II). A plot of the initial rate in mol/l. min *vs.* cyanide ion concentration is shown in Figure 3. The very slow *initial* rate of oxygen absorption in deficient cyanide concentration has already been discussed. Thus at KCN/AH⁺ ratios of up to 0.75 a

(10) G. A. Russell, A. J. Moye, E. G. Janzen, S. Mak, and E. R. Talaty, *J. Org. Chem.*, **32**, 137 (1967).
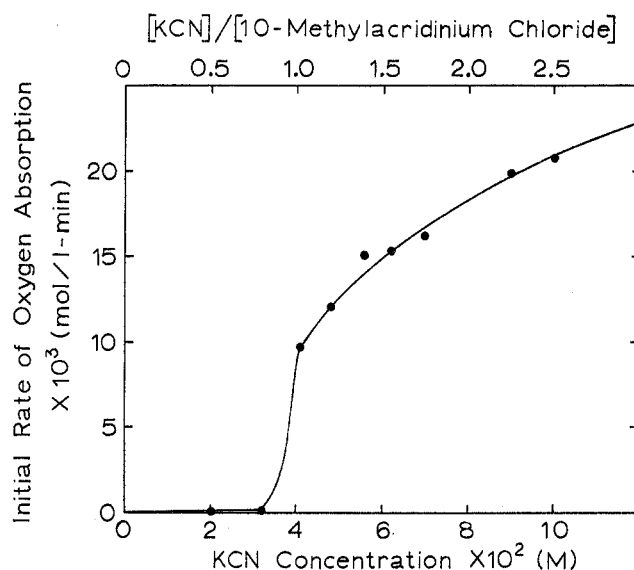

Figure 3.—Dependence of the initial rate of oxygen absorption on potassium cyanide concentration from solutions initially containing 0.0400 *M* *N*-methylacridinium chloride in 90% DMSO–10% water.

TABLE II

INITIAL RATE OF OXYGEN ABSORPTION[a]

[AH⁺Cl⁻],[b] *M*	[KCN], *M*	Initial rate, (mol/l. min)
0.0400	0.0202	0.00[c]
0.0400	0.0319	0.00[c]
0.0400	0.0410	0.0097
0.0400	0.0484	0.0121
0.0400	0.0558	0.0151
0.0400	0.0616	0.0153
0.0400	0.0696	0.0162
0.0400	0.0900	0.0199
0.0400	0.0998	0.0208

[a] Reactions run in 25 ml of 90:10 DMSO–water by volume and agitated by shaker. [b] AH⁺Cl⁻ = *N*-methylacridinium chloride. [c] Reaction mixture agitated by magnetic stirrer.

negligible amount of oxygen is absorbed compared to experiments where cyanide is in excess. This indicates that the rate of addition of cyanide to AH⁺ to produce AHCN is faster than the ionization of AHCN to ACN⁻ (if the assumption is made that the species reacting with oxygen is mainly ACN⁻). Since the first equivalent of cyanide produces AHCN rapidly the initial rate of oxygen uptake should depend on the remaining cyanide concentration. A first-order dependence on excess cyanide (KCN/AH⁺ > 1.00) would point to a rate-limiting formation of ACN⁻. The observed dependence on excess cyanide concentration shown in Figure 3 is not very encouraging. Although increasing the cyanide concentration does increase the initial rate of oxidation, the effect diminishes at higher KCN/AH⁺ ratios. This result is not understood at this time but may be a function of the activity and/or "basicity" of cyanide ion at these concentrations in 90% DMSO–10% water. Ion pairing effects may be operative and influential. Another possibility is that the rate of oxygen uptake has reached the rate of availability (*i.e.*, dissolution and diffusion) of oxygen but this appears unlikely from previous experience with this type of oxidation.[5,6,10]

The most logical oxidation mechanism appears to involve rapid addition of cyanide to give AHCN and a

slower rate-limiting ionization of AHCN to ACN⁻. This mechanism is not inconsistent with the data in Figure 3 and has precedence in the literature.[11,12]

The discussion up to this point has implied that the equilibrium constant for eq 1 is large, *i.e.*, AHCN is produced rapidly essentially quantitatively. That this is not entirely correct can be deduced from the rate of initial oxygen uptake at ratios of KCN/AH⁺ from 0.75 to 1.25. At a ratio of 1.0, a rapid rate of oxygen absorption is observed. It is apparent that a significant amount of cyanide ion is present in solution at these concentrations to effect ionization to ACN⁻. Moreover since a relatively high oxygen stoichiometry and yield of oxidized product (*N*-methylacridone) is realized (Table I) the cyanide ion appears to act in a catalytic capacity. This means that a base at least as effective as cyanide ion is produced in the oxidation. A likely candidate is the hydroperoxide anion probably produced in the oxidation of the carbanion. Since the pK_a's of alkyl hydroperoxides are somewhat smaller than the pK_a's of alcohols ($\sim$19) the hydroperoxide and cyanide anions are probably of comparable basicity in this solvent system (the K_a of HCN in water is 7.2×10^{-10}).

In this study only one solvent system was used (90% DMSO–10% water) because of solubility difficulties. The appreciable amount of water present will of course hydrolyze the cyanide ion and protonate the hydroperoxide anion. The expected leveling effect of water probably precludes detecting a difference in rates of oxygen uptake with bases of differing basicity. Although the hydroxide ion produced may be ionizing AHCN to ACN⁻[9,13] the almost quantitative isolation of AHCN from the addition of cyanide to AH⁺ in solutions deficient in cyanide (Table I) proves that hydroxide does not compete with cyanide in the addition to AH⁺ under such conditions.[14] Although product studies do not necessarily rule out the intermediacy of AHOH produced by hydroxide addition in the presence of excess cyanide, since *N*-methylacridone (NMA) is also the expected oxidation product in this case, the very clean 1:1 oxygen to product stoichiometry found (Table I) indicates that the secondary alcohol is probably not the major species oxidized.[15] However, the inability to obtain quantitative yields of NMA based on starting AH⁺ concentrations might be due to the production of a small amount of the alcohol. AHOH would be expected to oxidize very slowly by a chain mechanism (by analogy to benzhydrol[12]). A comparison of runs in Table I shows that an additional amount of oxygen is absorbed after 2 hr and the yield of NMA is

increased by 8% after 40 hr. The slight decrease in NMA yield with increase in cyanide concentration may also be significant since higher concentrations of cyanide ion would also produce higher concentrations of the hydroxide ion.

The results of Table I clearly show that 1 mol of oxygen produces 1 mol of NMA in the oxidation of AHCN. Since cyanate ion has been detected in the
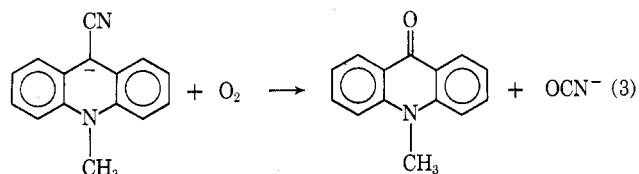
basic oxidation of diphenylactonitrile to benzophenone,[16] a search was made for this species in these oxidations. Solutions were diluted tenfold with water to precipitate NMA and tested for the presence of cyanate. The test was positive only for experiments run with highly concentrated solutions (see Experimental Section). Quantitative results were not obtained. The cyanide ion concentration remaining in the same filtrates was determined quantitatively however. These results support the postulated formation of cyanate ion since the sums of the cyanide ion and NMA concentrations (the concentration of cyanate should be equal to the concentration of NMA according to eq 3) are within 10% of the total amount of cyanide added to the solution: 1.43, 1.50, and 1.67 mmol/25 ml, respectively (Table I). Our data thus supports the cyanate stoichiometry in eq 3. The overall reaction is
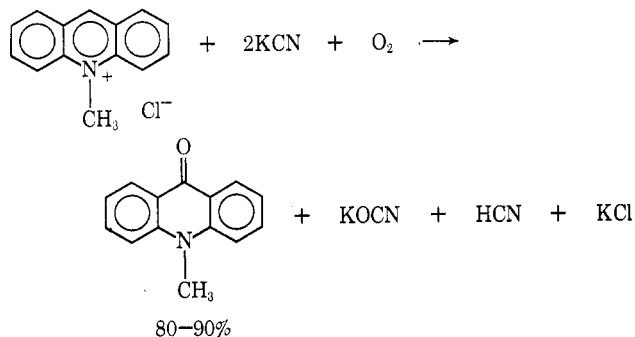
N-Methyl-9-cyanoacridanyl Radical.—Solutions of AH⁺ containing excess cyanide ion exposed to oxygen produce the highest concentrations of ACN· observed. Thus, the addition of excess KCN to 2.00×10^{-2} *M* AH⁺ in 90% DMSO–10% water gave 2.96×10^{-4} *M* ACN· (1.5%). However, the lifetime of the radical under such conditions is less than 2 min. In fact the time period wherein ACN· is most readily detectable in solutions through which oxygen is continuously bubbled correlates well with the time period for maximum oxygen absorption (Figure 2). For studies of the radical over more extended periods of time (*e.g.*, for obtaining esr spectra at high resolution), a solution originally saturated with air closed to further oxygen exposure provides a reasonable concentration of radicals stable over a period of many hours.

(11) G. A. Russell and A. G. Bemis, *J. Amer. Chem. Soc.*, **88**, 5491 (1966).

(12) G. A. Russell, A. G. Bemis, E. J. Geels, E. G. Janzen, and A. J. Moye, *Advan. Chem. Ser.*, **75**, 174 (1968).

(13) AHCN is known to be oxidized in alkaline ethanol to *N*-methyl-acridone: (a) F. McCapra, D. G. Richardson, and Y. C. Chang, *Photochem. Photobiol.* **4**, 111 (1965); (b) F. McCapra and D. G. Richardson, *Tetrahedron Lett.*, **43**, 3167 (1964).

(14) The formation of *N*-methyl-9-hydroxyacridan from the nucleophilic addition of hydroxide ion to *N*-methylacridinium bromide is known to be slow in polar solvents as determined by uv studies and the equilibrium appears to favor *N*-methylacridinium hydroxide: R. M. Acheson and L. E.

$$AH^+ Br^- + OH^- \rightleftharpoons AH^+ OH^- \rightleftharpoons AHOH$$

Orgel, "Acridines," Interscience, New York, N. Y., 1956, p 281; A. Albert, "The Acridines," St. Martin's Press, New York, N. Y., 1966, p 540.

(15) Weak carbon–acid alcohols (*e.g.*, benzhydrol) oxidize to ketones with relatively high oxygen stoichiometries ($\sim$1.5).[12] The oxidation of AHOH–aqueous DMSO would be expected to behave similarly.

(16) H. G. Aurich, *Tetrahedron Lett.*, **12**, 657 (1964); B. R. Garrett, Ph.D. Thesis, University of Delaware, Newark, Del., 1959, in A. J. Moye, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1961.

The most reasonable oxygenation mechanism consistent with the stoichiometry of eq 3 and the relatively low yield of radical detected is an electron transfer oxidation of ACN⁻ by O_2 to give a radical superoxide pair. Most of the product probably arises from collapse of this radical pair after spin relaxation to produce the peroxy anion. The formation of detectable concentrations of ACN· radicals could be the result of dissociation of the caged radical pair. The reaction of

$$(4)$$
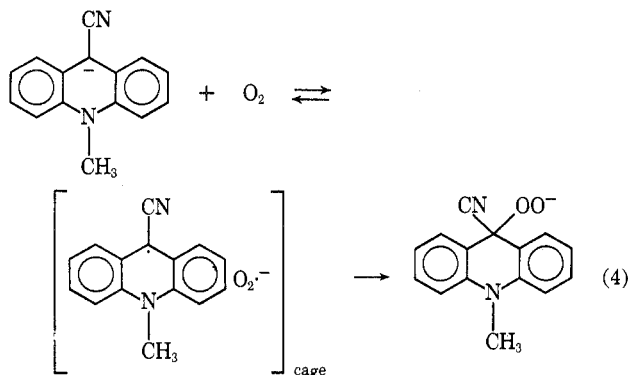
ACN· with oxygen should produce the peroxy anion *via* the peroxy radical by a chain electron transfer oxidation.

$$(5)$$

$$(6)$$
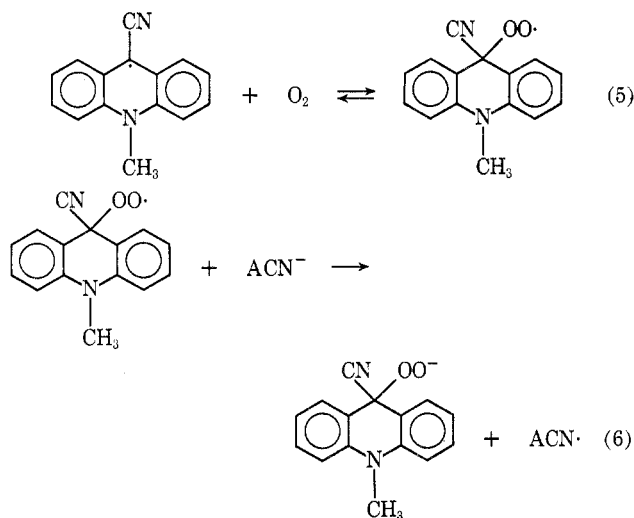
Numerous experiments with varying amounts of oxygen failed to detect the intermediate peroxy radicals. Only on one occasion a low-field signal was obtained in addition to the spectrum of ACN· which might have been due to the peroxy radical but this result could not be reproduced.

Neutral radicals presumably produced in the oxygen electron transfer oxidation of carbanions are usually not detected by esr. This is probably due to a very rapid rate of reaction of oxygen with the radicals and a large equilibrium constant favoring the peroxy radical (eq 5). The existence of a temperature dependent equilibrium between a peroxy radical and the corresponding radical plus oxygen was suspected for some time[17] and has been demonstrated for triphenylmethyl radical in the solid state.[18] Other examples of the

detection of neutral stable free radicals in the oxygenation of stable carbanions are Koelsch's radical (I),[19] phenalenyl (II),[20] and tris-*p*-nitrophenylmethyl (III).[5,21] In these cases and in the case of ACN· the rate of eq 5 must be relatively slow and the equilibrium must favor the carbon radical. Rapid carbon radical producing reactions (4 and 6, particularly 6) are obviously necessary for radical detection. The reversibility of reactions 4 or 6 for ACN· has not been demonstrated although this possibility for reaction 4 seems reasonable.

In comparing the esr detectability of neutral radical intermediates in the oxygenation of carbanions of weak carbon acids ($pK_a \simeq 20\text{-}25$) the reaction most likely to be crucial in determining the "stability" of the radical to oxygen is reaction 5 since the rates of reaction 4 and 6 probably do not vary markedly with change in structure within this pK_a range. The equilibrium constant for reaction 5 must depend solely on the delocalization stability of the radical since the intrinsic thermodynamic stability of the peroxy radical will be almost the same regardless of the structure of the radical. The unusual stability of ACN· may be due to sizable delocalization of the unpaired electron onto the nitrogen
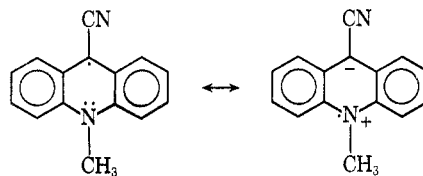
atom. The spin density on nitrogen is 0.127 (estimated from MO calculations and nitrogen hyperfine coupling) whereas the spin density on C-9 is only approximately 0.3. The only good system available for comparison is the 9-xanthyl radical system.[22] Unfortunately, analogous derivatives have not been studied. Vincow and coworkers have not made 9-cyanoxanthyl radical and we have not studied the *N*-methyl-9-phenylacridanyl. A study of the comparitive stability of these radicals to oxygen would appear to be worth while.

Chemiluminescence.—Oxygenation of the cyanide ion addition product of AH⁺ is a chemiluminescent reaction. When excess KCN is added to a solution of AH⁺ the color of the solution turns from yellow to red. The oxygen uptake is rapid at this time and a blue glow is visible in the dark. Finally the color of the solution is yellow with a green fluorescence. The chemiluminescence spectrum shows a maximum at 442 mμ. Since the fluorescence spectrum of *N*-methylacridone has a maximum at 440–442 mμ in a variety of solvents,[13,23,24] this compound is implicated as the light emitter. This conclusion has been reached by others[13] in the NH_4OH/H_2O_2 or OH^-/O_2 aqueous ethanol-*N*-methyl-9-cyanoacridinium nitrate systems for the same reasons.

A typical plot of the relative light intensity as a function of time is given in Figure 4. The initial slope

(17) (a) G. A. Russell in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience, New York, N. Y., 1962, p 110; (b) D. G. Hendry and G. A. Russell, *J. Amer. Chem. Soc.*, **86**, 2371 (1964).

(18) C. L. Ayers, E. G. Janzen, and F. J. Johnston, *ibid.*, **88**, 2610 (1966); E. G. Janzen, F. J. Johnston, and C. L. Ayers, *ibid.*, **89**, 1176 (1967).

(19) J. G. Pacifici, J. F. Garst, and E. G. Janzen, *ibid.*, **87**, 3014 (1965).

(20) D. H. Reid, *Chem. Ind. (London)*, 1504 (1956); *Tetrahedron*, **3**, 339 (1958).

(21) M. F. Hawthorne and G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 2549 (1955).

(22) M. D. Sevilla and G. Vincow, *J. Phys. Chem.*, **72**, 3641, 3647 (1968).

(23) J. R. Totter, *Photochem. Photobiol.*, **3**, 231 (1964); A. S. Van der Burg, *Recl. Trav. Chim. Pays-Bas*, **69**, 1525 (1950).

(24) M. M. Rauhut, D. Sheehan, R. A. Clarke, B. G. Roberts, and A. M. Semsel, *J. Org. Chem.*, **30**, 3587 (1965); K. D. Legg and D. M. Hercules, *J. Amer. Chem. Soc.*, **91**, 1902 (1969).

of light emission vs. time and the time for the emission to reach its maximum varies with exposure to oxygen, i.e., agitation of the solution. However, it is clear that the major portion of the oxygen is absorbed in the initial stages of the reaction during the time when the rate of increase of light emission is greatest (compare Figures 2 and 4). It was thus of interest to compare the relative light intensity and uptake of oxygen profiles. Both the uptake of oxygen and the relative light intensity were monitored simultaneously for a stirred 0.04 M AH$^+$ solution containing 0.062 M KCN initially. The time profiles are identical for the first minute of the reaction (Figure 5) and the maximum relative light intensity occurs at the same time as the break in the oxygen absorption time curve (Figure 5). This result shows that the steps between the oxygen absorption reaction and the NMA* precursor are either very fast or the same one; i.e., the reaction with oxygen may produce the precursor to NMA* directly. Moreover, it appears that the NMA* precursor has a reasonable lifetime since light emission continues although at a diminishing level for a relatively long period after the maximum intensity point is reached (Figure 5).

A plot of the maximum relative intensity of light emission during oxidation as a function of added cyanide ion is shown in Figure 6. Very low light intensities are detected in the oxidation of AHCN in the absence of excess cyanide (KCN/AH$^+$ ratios of <0.75, indicated as A on plot) which is consistent with the negligible oxygen uptake observed under such conditions (Figure 3).[25]

(25) Further experiments show that a chain autoxidation of AHCN to produce chemiluminescence cannot be initiated with free-radical initiators.
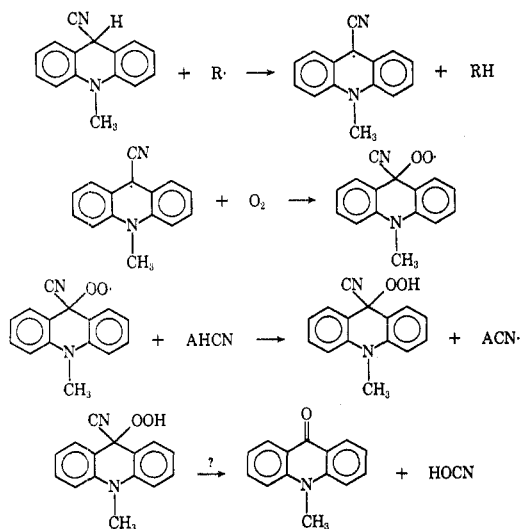
Thus azobisisobutyronitrile or phenylazotriphenylmethane, sources for 2-cyanopropyl or phenyl radicals, produce only low levels of light in solutions of AHCN in DMSO, toluene, or ethanol at 30, 55, or 70° exposed to various amounts of oxygen. This observation is not unprecedented. Tris-p-nitrophenylmethane is totally inert to radical-initiated autoxidation[21] and triphenylmethane is itself rather inert to autoxidation reactions.[17b] The inability of these compounds to sustain an autoxidation reaction is attributed to the slow reaction of the carbon radical with oxygen [G. A. Russell, J. Amer. Chem. Soc., 78, 1047 (1956)]. This observation is of interest for another reason. It has been suggested that certain compounds might serve as radical detectors by emitting light when in the presence of free radicals [J. R. Totter, V. J. Medina, and J. L. Scoseria, J. Biol. Chem., 235, 238 (1960); J. R. Totter, E. C. de DuGros, and C. Riveiro, ibid., 235, 1839 (1960); J. R. Totter, W. Stevenson, and G. E. Philbrook, J. Phys. Chem., 68, 752 (1964)]. Since sensitive equipment for the detection of small amounts of light is readily available, this technique might provide greater sensitivity
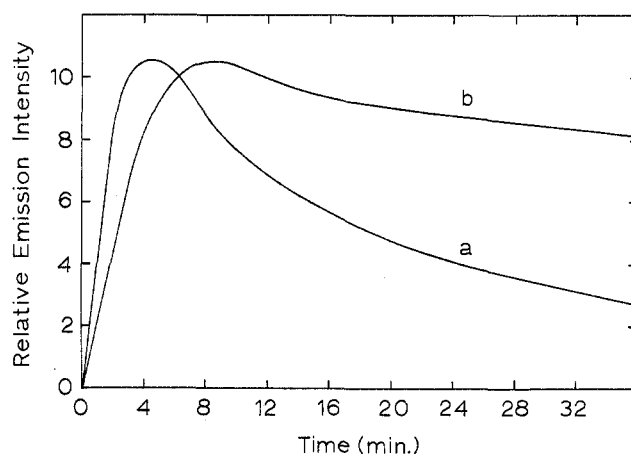

Figure 4.—Relative emission intensity as a function of time for (a) 0.017 M N-methylacridinium chloride and 0.021 M potassium cyanide, and (b) 0.012 M lucigenin (DBA^{2+}) and 0.021 M potassium cyanide in 90% DMSO–10% water through which oxygen was continuously bubbled.
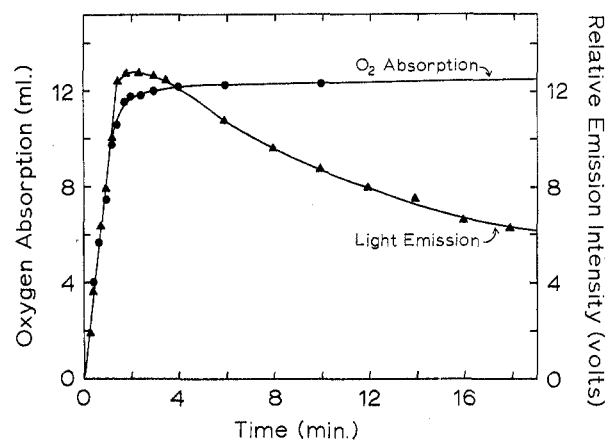

Figure 5.—Oxygen absorption (left scale) and relative light emission (right scale) as a function of time measured simultaneously from a stirred solution initially containing 0.04 M N-methylacridinium chloride and 0.062 M potassium cyanide.

Chemiluminescence becomes appreciable after the ratio of KCN to AH$^+$ exceeds 0.75. The maximum relative intensity increases thereafter as a function of cyanide ion concentration. The shape of this plot is remarkably similar to the plot of the initial rate of oxygen uptake as a function of cyanide ion (Figure 3). The plots are almost superimposable using the same KCN/AH$^+$ ratios up to a ratio of 1.50 (indicated as B on plot). Thereafter the maximum emission intensity continues to increase with increase in cyanide ion concentration (indicated as C on plot) although the initial rate of oxygen uptake levels off.

The fact that the initial rates of oxygen uptake show the same dependence on excess cyanide ion concentration as the relative maximum light intensities (Figures 3 and 6) provides further support for the conclusion that the concentration of the NMA* precursor depends directly on the concentration of the species reacting with oxygen.

than, for example, esr spectrometry. The autoxidation of AHCN might have served as such a system if the detection of radicals could be reliably based on the initiation of an efficient chemiluminescent chain reaction.
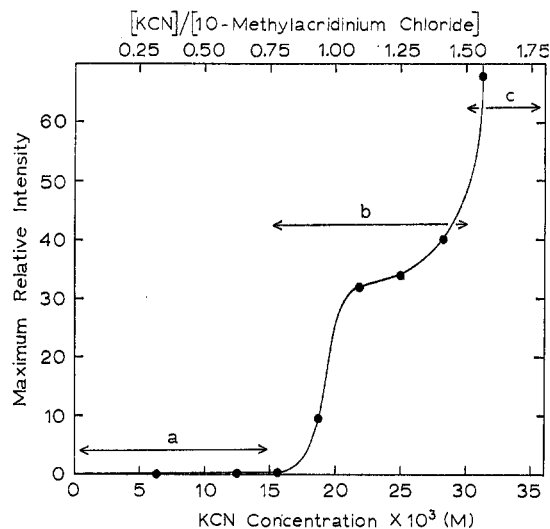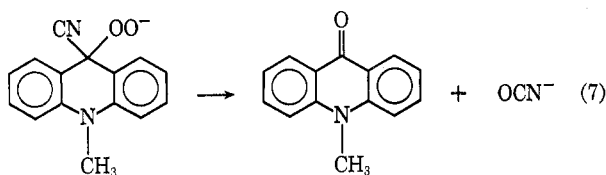
Figure 6.—Dependence of the maximum chemiluminescence emission intensity on potassium cyanide concentration from solutions initially containing 0.020 M N-methylacridinium chloride in 90% DMSO–10% water.

The major and only isolated product in these oxidations is N-methylacridone. It is probably produced from the hydroperoxide or hydroperoxide anion. The


detection of cyanate and the quantitative determination of cyanide remaining after the reaction, rule out the following product-forming route.
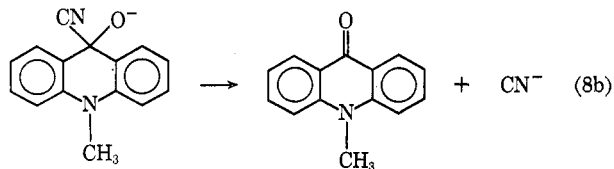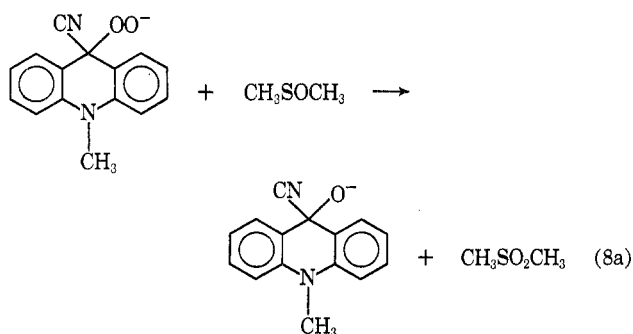

There is precedence for the involvement of DMSO in the basic oxygenation of triphenylmethane.[11] Thus triphenylmethyl hydroperoxide is converted to the carbinol in 94% yield with production of dimethyl sulfone in the presence of base in DMSO. If this reaction is fast it can be concluded that eq 7 must proceed considerably faster than eq 8 or a stable intermediate peroxide ion exists which is inert to DMSO. A mechanism previously proposed for product and excited-state

formation in these and similar chemiluminescent reactions involves a four-membered peroxide ring.[13,26]
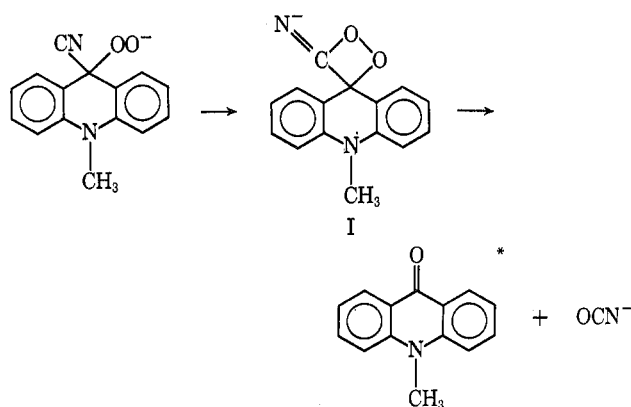

The lifetime of I, if an intermediate, is not known since evidence for the existence of this molecule has not been reported by those who proposed its structure. It would appear to fill the requirements necessary as a final intermediate in the oxygenation of AHCN in our system, since it might be more stable to DMSO than a free peroxide anion. If I is in fact the precursor to NMA* it must be reasonably long lived since light emission is seen for quite a long period after most of the oxygen is absorbed (Figure 4).

However, the chemiluminescence results could be rationalized in terms of another scheme. Two probable products in reactions producing stable radicals in the presence of oxygen are dimers and peroxides. The formation of these side products is certainly possible in this system particularly because of the relatively high concentrations of ACN· radicals produced during the oxygen uptake. If the decomposition of the peroxide
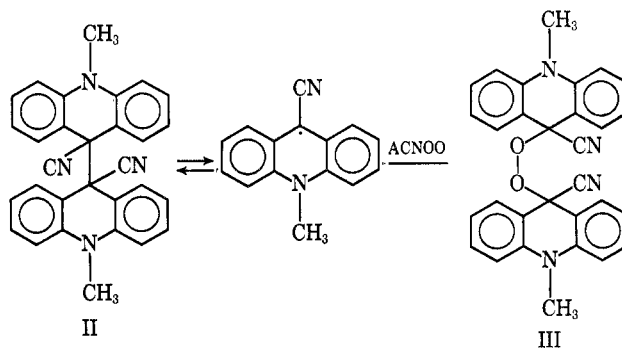
III is chemiluminescent the maximum light intensity observed would be a function of the concentration of III
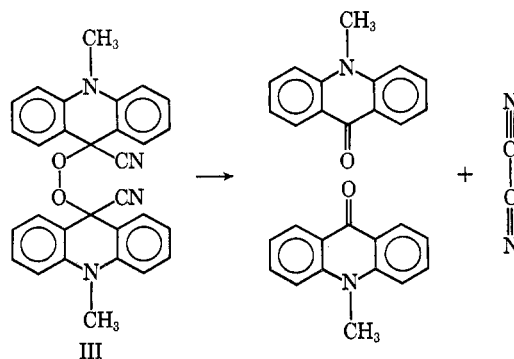
(26) See, however, M. M. Rauhut, *Accounts Chem. Res.*, **2**, 80 (1969).

which in turn would depend on the steady-state concentrations of ACN· and A(CN)OO·. Since an increase in cyanide concentration increases the rate of oxygen uptake and thus the steady-state concentrations of ACN· and A(CN)OO· the concentration of III should increase with increase in cyanide concentration as observed.

An additional possibility is the storage of ACN· radicals as the dimer, II. The dimer might be expected to dissociate relatively slowly to ACN· radicals and in the presence of oxygen more of the peroxide III would be produced. The concentration of II would depend on the concentration of ACN· present during the oxygenation which itself would be dependent on the cyanide ion concentration.

A test for the possible involvement of the dimer in the chemiluminescence step was attempted. Previous experiments have shown that the addition of cyanide ion to lucigenin produces esr detectable amounts of ACN· radicals.[2] The addition of cyanide to lucigenin in the presence of oxygen *does* produce chemiluminescence which has a time profile not too different from that observed with cyanide and AH⁺ (Figure 4). Thus mechanisms which incorporate A(CN)OO· radicals in the chemiluminescence scheme have some support. In addition to the reaction of A(CN)OO· and ACN· to produce the peroxide III, one might expect the reaction of two peroxy radicals to be possible. The formation of

$$2A(CN)OO. \longrightarrow A(CN)OOOO(CN)A$$
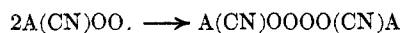
short-lived tetroxides and their decomposition to give oxygen and the corresponding oxy radicals has been extensively studied recently.[27] In this case the decomposition should be chemiluminescent and should produce cyano radicals and oxygen (or cyanato radicals) in addition to excited *N*-methylacridone.

The possibility of using this reaction (*i.e.*, lucigenin plus cyanide ion in oxygen) to study this aspect of the

reaction quantitatively is unfortunately limited by the apparent tendency of cyanide to reduce this highly electrophilic compound by electron transfer giving presumably cyano radicals and the radical cation of lucigenin by analogy to observations made on similar compounds.[28] A product study of a cyanide addition-oxygenation experiment gave 60% *N,N'*-dimethyl-9,9'-biacridylidene (V), the product of a two-electron reduction of lucigenin.

IV

V
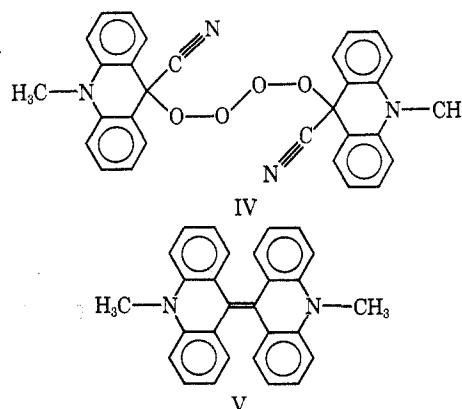
No comment has been made on the fact that increasing the cyanide ion concentration past a ratio of 1.50 (indicated as portion C on Figure 6) serves to increase further the maximum intensity of light emission although the initial rate of oxygen increases very little with increase in cyanide concentration after this point. No explanation for this observation is obvious although a cyanide ion induced decomposition of the peroxide III is suggested. The chloride ion reduction of benzoyl peroxide has recently been studied[29] and could be considered analogous to the proposed possible reaction.

Registry No.—*N*-Methylacridinium chloride, 5776-39-6; KCN, 151-50-8; AHCN, 837-43-4; NMA, 719-54-0.

(27) P. D. Bartlett and G. Guaraldi, *J. Amer. Chem. Soc.*, **89**, 4799 (1967); P. D. Bartlett and P. Gunther, *ibid.*, **88**, 3288 (1966); N. A. Miles and G. G. Arzoumanidis, *Chem. Ind. (London)*, 67 (1966).

(28) L. Papouchado, R. N. Adams, and S. W. Feldberg, *J. Electroanal. Chem.*, **21**, 410 (1969).

(29) N. J. Bunce and D. D. Tanner, *J. Amer. Chem. Soc.*, **91**, 6096 (1969).