(12) Gerald A. Segal, "Electronic Structure Calculation", Plenum Press., New York and London, P. 69-103, 1977.

(13) Quantum Chemistry Program Exchange, Indiana University (1975).

Quantitative Determination of Acetone formed in the Thermal and Photochemical Decompositions of Azobisisobutyronitrile

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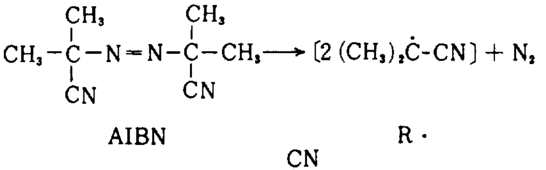
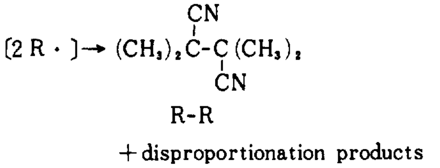
Cyanoisopropyl radical derived from azobisisobutyronitrile (AIBN) by either thermolysis or photolysis reacts with oxygen to give cyanoisopropylperoxy radical which then was converted to acetone and cyano radical and/or acetyl cyanide and methyl radical. Of these products, acetone formed was quantitatively determined by the addition of thianthrene cation radical perchlorate to the reaction mixture. The results showed that 55.7 mmol, 16.9 mmol, and 16.0 mmol of acetone were formed for 7 hours from 1 mol of AIBN at 82 ± 1°C in acetonitrile, carbon tetrachloride, and benzene, respectively. However, 22.2 mmol of acetone was formed from photolysis of 1 mmol of AIBN in acetonitrile. The value decreased to 13.2 mmol by bubbling argon into the solvent prior to photolysis.

Introduction

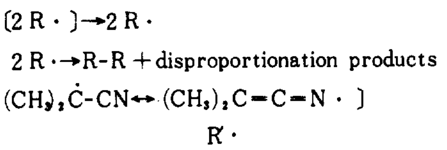
Thermal decomposition of AIBN under a degassing condition produces cyanoisopropyl radicals in pair, which then undergo a variety of reactions as shown in the following equations.



$$\underset{\text{AIBN}}{CH_3-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-CH_3} \longrightarrow \underset{R\cdot}{[2(CH_3)_2\dot{C}\text{-}CN]} + N_2 \tag{1}$$



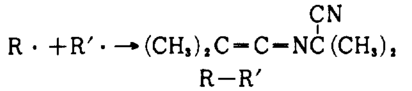
$$[2R\cdot] \rightarrow \underset{R\text{-}R}{(CH_3)_2\overset{CN}{C}\text{-}\underset{CN}{C}(CH_3)_2} + \text{disproportionation products} \tag{2}$$



$$[2R\cdot] \rightarrow 2R\cdot$$

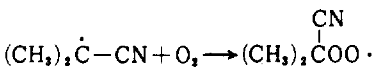
$$2R\cdot \rightarrow R\text{-}R + \text{disproportionation products} \tag{3}$$

$$\underset{R'\cdot}{[(CH_3)_2\dot{C}\text{-}CN \leftrightarrow (CH_3)_2C=C=N\cdot]}$$

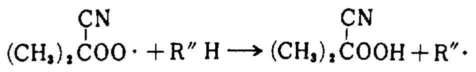


$$R\cdot + R'\cdot \rightarrow \underset{R-R'}{(CH_3)_2C=C=N\overset{CN}{C}(CH_3)_2} \tag{4}$$

The coupling product, tetramethylsuccinonitrile (R-R) is formed in the solvent cage or outside of the solvent cage as shown in eqs. (2) and (3), respectively. In the meantime, cyanoisopropyl radical is scavenged efficiently by oxygen molecule. The peroxy radicals thus formed have been reported to immediately become hydroperoxide and other products (eqs. 5,6)[1,2] whose pathways strongly depended on the hydrogen atom donor.

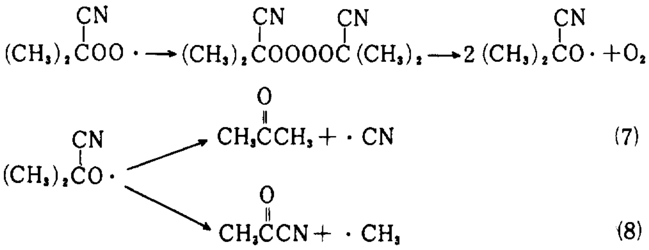


$$(CH_3)_2\dot{C}-CN + O_2 \longrightarrow (CH_3)_2\overset{CN}{C}OO\cdot \tag{5}$$



$$(CH_3)_2\overset{CN}{C}OO\cdot + R''H \longrightarrow (CH_3)_2\overset{CN}{C}OOH + R''\cdot \tag{6}$$

In the case of the absence of good hydrogen atom donor, it is expected that cyanoisopropylperoxy radical undergoes different reactions.[3] By the analogy with the cleavage mode of *t*-butylperoxy radical,[3] two kinds of cleavage reactions appear in mind. That is, dimerization, followed by the extrusion of oxygen molecule to give cyanoisopropoxy radical which then undergoes α scission to give either acetone and cyano radical (eq. 7) or acetyl cyanide and methyl radical (eq. 8).



$$(CH_3)_2\overset{CN}{C}OO\cdot \longrightarrow (CH_3)_2\overset{CN}{C}OOOO\overset{CN}{C}(CH_3)_2 \longrightarrow 2(CH_3)_2\overset{CN}{C}O\cdot + O_2$$

$$(CH_3)_2\overset{CN}{C}O\cdot \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_3 + \cdot CN \tag{7}$$

$$(CH_3)_2\overset{CN}{C}O\cdot \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CN + \cdot CH_3 \tag{8}$$

To our knowledge, no such investigation on cyanoisopropylperoxy radical has been made. In order to determine quantitatively the amount of acetone formed was used thianthrene cation radical perchlorate which has been reported to react quantitatively with acetone to give 5-acetonylthianthrenium perchlorate.[5]

Experimental

AIBN was from Merck and was recrystallized from absolute ethanol. Thianthrene and thianthrene cation radical perchlorate were prepared by the methods described elsewhere.[6] Acetonitrile was Kanto Chemical Corporation Extra Pure and was refluxed with phosphorus pentoxide for three hours. By redistilling the first distillate was obtained dried acetonitrile. Nitrogen and argon gases were purchased from Korea Helium Company. The former was dried by passage through calcium chloride tube, followed by conc. sulfuric acid and the latter was passed through Hydrox Purifier (Mallinckrodt, Model No. 8301) to remove oxygen completely.

Column chromatography was performed with Merck silica gel (70-230 ASTM mesh, 0.063-0.2 mm). All chromatographic solvents were distilled prior to use. Ultraviolet spectra were obtained with a Beckman 5270 spectrometer. Infrared spectra were obtained using a Perkin-Elmer 283 infrared spectrometer. All infrared spectra were taken using potassium bromide pellets, unless otherwise indicated. ^{1}H NMR spectra were recorded on a Varian EM-360A spectrometer and chemical shifts were relative to tetramethylsilane. Gas chromatography was accomplished with a Hitachi-164 gas chromatograph.

General Procedure for the Thermolysis of AIBN. About 6 mmol of AIBN was dissolved in 50 *ml* of acetonitrile. The solution was refluxed at 82 ± 1°C for 7 hours with stirring, followed by cooling to 0°C in an ice-water bath. To the cooled solution was added about 4 mmol of thianthrene cation radical perchlorate and the mixture was stirred at room temperature for 14 hours. The unreacted thianthrene cation radical perchlorate was completely destroyed with the minimum quantity of water by which time the dark purple color of the cation radical completely disappeared. After the solvent was removed on a rotary evaporator, the residue was chromatographed on a silica gel column. After a successive elution with benzene (1.5 L), chloroform (1 L), and ether (0.7 L), elution with ethyl acetate (0.8 L) gave 5-acetonylthianthrenium perchlorate, which was dissolved in 15 m*l* of acetonitrile. To this solution were added 1 m*l* of water and excess of tetrabutylammonium iodide. After the mixture was stirred at room temperature for 8 hours, the solvent was removed on a rotary evaporator and the residue was chromatographed on a silica gel column. Elution with hexane (0.6 L) gave thianthrene. By measuring the amount of thianthrene, one may calculate the amount of acetone formed during the course of AIBN thermolysis.

In the case of thermolysis of AIBN in carbon tetrachloride, the mixture was refluxed for 7 hours, followed by the addition of about 60 *ml* of acetonitrile. To this solution was added thianthrene cation radical perchlorate. The mixture was stirred and worked up as described in the thermolysis in acetonitrile solvent.

The same procedure was applied to the case where benzene was used as a solvent.

General Procedure for the Photochemical Decomposition of AIBN. About 0.7 mmol of AIBN was measured precisely and placed in a KIMAX test tube containing 5 *ml* of acetonitrile. After AIBN was completely dissolved, the test tube was capped with a rubber septum. Thus made 8 test tubes were fitted on a merrygo-round having filter glasses (ACE GLASS, Cat. No. 7891-42) and irradiated for 3 hours with 450 W Ace-Hanovia medium pressure mercury lamp in a quartz immersion well which was cooled by circulating a cooling water of 5.5°C. Then each test tube was cooled in an ice-water bath, followed by the addition of 0.35 mmol of thianthrene cation radical perchlorate in each test tube. The test tubes were equipped on a shaker for 24 hours. The combined mixture was worked up as described in the thermolysis procedure.

Reaction of thianthrene cation radical perchlorate with acetyl cyanide.

Preparation of Acetyl Cyanide. The title compound was prepared from the reaction of acetyl chloride with copper (I) cyanide in benzonitrile according to the reported method.[7] The reaction mixture was distilled and fractions distilled at 80-100°C were collected. The fractions were consisted of acetyl chloride, acetyl cyanide, and benzonitrile. Acetyl chloride was removed on a rotary evaporator without using bath. Acetyl cyanide was collected in the trap of the rotary evaporator using warmed water bath (50°C) and redistilled prior to use. It deteriorates slowly and tints brown color.

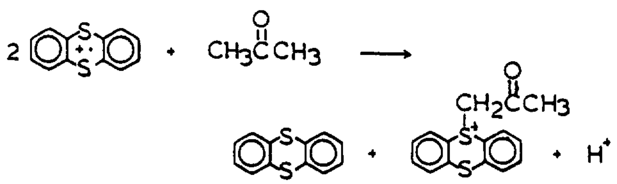
Reaction with Acetyl Cyanide. To a stirred solution of 0.701 g (2.22 mmol) of thianthrene cation radical perchlorate in 30 mL of acetonitrile was added 0.18 mL (2.54 mmol) of acetyl cyanide. The mixture was stirred at room temperature for about a month by which time a purple color of the cation radical disappeared. Tlc (CH_2Cl_2) showed four sports with R_f values of 0.86, 0.37, 0.29, and 0. These spots corresponded to thianthrene, thianthrene 5-oxide, cis-thianthrene-5, 10-dioxide, and inorganic salts, respectively, and identified on the spectroscopic data[8] after column chromatography.

In addition, 0.5 g (2.94 mmol) of silver nitrate and 30 mL of water were added to the reaction mixture. The precipitate was filtered and washed successively with benzene (100 mL), methylene chloride (100 mL), acetone (100 mL), and water (100 mL). Infrared spectrum of remained solid was taken on KBr plate using n-decane and showed a band at 2165 cm^{-1}, probably due to AgCN (lit[9]. 2138 cm^{-1}).

Reaction with 4-Methyl-2-oxo-pentanenitrile. To a stirred solution of 0.145 g (0.46 mmol) of thianthrene cation radical perchlorate in 40 mL of acetonirile was added 0.3 mL (2.67 mmol) of 4-methyl-2-oxo-pentanenitrile. The dark purple color of the cation radical disappeared completely in 60 hours. Tlc (benzene) showed three spots corresponding to thianthrene, thianthrene 5-oxide, and *cis*-thianthrene-5, 10-dioxide. These compounds along with 3-methylbutanoic acid which was a convereted product of 4-methyl-2-oxo-pentanenitrile were isolated by the column chromatography. 3-Methylbutanoic acid; ^{1}H NMR (CCl_4): δ 0.98 (d, 6H, $2CH_3$), 2.25 (d, 2H, CH_2), 1.91 (m, 1H, CH), 9.77 (s, 1H, COOH); IR (neat): 3300 (O-H stretch), 1710 (C=O stretch) cm^{-1}.

Results and Discussion

It has been known that thianthrene cation radical perchlorate reacts with acetone to give 5-acetonylthianthrenium perchlorate according to the following stoichiometry.[5]



5-Acetonylthianthrenium perchlorate can be readily separated from the reaction mixture by column chromatography. However, since the perchlorate salt is attacked by a variety of nucleophiles in solution to lead thianthrene and monosubstituted acetone,[5]

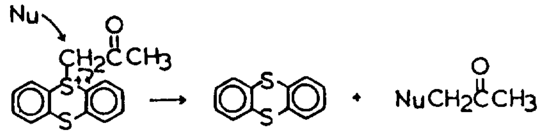


TABLE 1: Acetone Formed from the 7 Hours Thermolysis of 1 Mole of AIBN at 82±1°C

Solvents	Acetone (mmol)
Acetonitrile	55.7
Carbon tetrachloride	16.9
Benzene	16.0

dried solvents are required during the course of column chromatography and it is more reliable to determine the amout of thianthrene rather than that of the salt in order to measure the amount of acetone formed.

Thermolysis of AIBN in the air for 7 hours at 82°C corresponds to about 6 half-life periods[2] by which time small amount of AIBN is still present. Table 1 summarizes the results and shows that different amount of acetone is produced in different solvents.

This is the first demonstration on the acetone formation from cyanoisopropyl radical. We did not attempt to investigate the fate of CN· which could be concomitantly formed by the α-cleavage of cyanoisopropyloxy radical. On the other hand, the possible formation of acetyl cyanide, followed by the reaction with thianthrene cation radical, yielding to 5-(2-cyano-2-oxoethyl)thianthrenium perchlorate was checked by using thianthrene cation radical perchlorate and acetyl cyanide independently synthesized. Synthesis of acetyl cyanide was tried at various conditions: Reaction of acetyl chloride with copper (I) cyanide without using any solvent gave only less than 5% yield of the product; in the presence of acetonitrile solvent it was difficult to separate the product from the solvent in spite of a slight increase in yield. Using KI and CuCN in methylene chloride[10] was obtained much poor yield of the product than in acetonitrile. The desired product was obtained in benzonitrile according to the reported method.[7]

Reaction of acetyl cyanide with thianthrene cation radical did not afford the product associated with thianthrene. Instead, only thianthrene, thianthrene 5-oxide, *cis*-thianthrene-5, 10-dioxide were obtained. Of these products, it is particularly interesting to observe the formation of only one geometrical isomer, *cis*-thianthrene-5, 10-dioxide. As proposed in the other work performed in this laboratory,[8] the formation of *cis*-dioxide can be explicable in the following fashion:

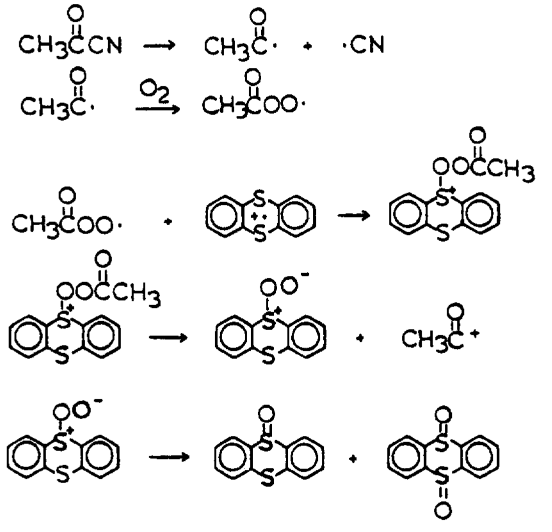


TABLE 2: Acetone Formed from the Photolysis of 1 Mole of AIBN

Solvents	Acetone (mmol)	Reaction time (hours)
Acetonitrile	22.2	3
Acetonitrile	22.2	5
Acetonitrile[a]	22.2	5
Acetonitrile[b]	13.2	5
Acetonitrile[c]	22.2	5

[a] saturated with oxygen. [b] saturated with argon. [c] The reaction mixture was cooled in a dry ice-acetone bath before the addition of the cation radical.

The acetylium ion is believed to convert into acetic acid. The results obtained by Hirbert and Satchell[11] on the hydrolysis reaction of acetyl cyanide show that pyruvic acid is formed under the high acidic condition and high concentration (3 mol) of acetyl cyanide. However, in neutral or slightly acidic solution hydrolysis proceeded rapidly to give acetic acid and hydrogen cyanide which was confirmed by the isolation of silver cyanide. This technique was applied to the reaction mixture of the reaction of thianthrene cation radical perchlorate with authentic acetyl cyanide. Addition of aqueous silver nitrate to the reaction mixture gave precipitates which were successively washed with organic solvents and water yielding small amount of solid exhibiting a band at 2165 cm^{-1}. This result indicated that hydrolysis to hydrogen cyanide and acetic acid indeed occurred. Conversion of 4-methyl-2-oxo-pentanenitrile to 3-methylbutanoic acid under the same condition as in the reaction with acetyl cyanide fortifies the view on the prior hydrolysis of nitrile to the reaction with thianthrene cation radical. In the meantime, attempt to detect pyruvic acid by GC has been unsuccessful. Therefore, it can be concluded that acetyl cyanide that might be formed undergoes either hydrolysis to give acetic acid and hydrogen cyanide or homolytic decomposition to give acetyl and cyano radicals prior to the reaction with thianthrene cation radical perchlorate.

In the case of photolysis of AIBN in acetonitrile, it appeared that acetone was formed in a lesser amount than in the thermolysis. Table 2 shows the results.

Studies in benzene and carbon tetrachloride were troublesome because of the solubilities. The same amounts of acetone was obtained from either 3 hours- or 5 hours-irradiation, which supported complete decomposition of AIBN. It appeared that the formation ratio of acetone to AIBN remained unchangeable in spite of the bubbling of oxygen gas into the solvent. This result implies that the solvent contains enough amount of oxygen to react with cyanoisopropyl radical. On the other hand, expelling oxygen from the solvent using argon gas, followed by photolysis gave 13.2 mmol of acetone per 1 mole of AIBN, which was ca. 41% decreased value in comparison with that obtained without using argon gas. Cooling the reaction vessel in a dry ice-acetone bath, followed by the addition of thianthrene cation radical perchlorate did not change the ratio of acetone to AIBN.

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References

(1) C.E. Boozer, G.S. Hammond, C.E. Hamilton, and J.N. Sen, *J. Amer. Chem. Soc.*, **77**, 3233(1955).

(2) G.S. Hammond, J.N. Sen, and C.E. Boozer, *J. Amer. Chem. Soc.*, **77**, 3244 (1955).

(3) D.C. Nonhebel and J.C. Walton, Free-radical Chemistry, Cambridge, Chap. 10, p. 399, 1974.

(4) T. Miller and R.S. Stringham, *J. Amer. Chem. Soc.*, **90**, 1062(1968).

(5) K. Kim and H.J. Shine, *Tetrahedron Lett.*, 4413(1974).

(6) S.H. Kim and K. Kim, *J. Korean Chem. Soc.*, **25**, 383(1981).

(7) J.F. Normant and C. Piechucki, *Bull. Soc. Chim. Fr.* 2402(1972).

(8) J. Shin and K. Kim. *Bull. Korean Chem. Soc.*, **5**, 211(1984).

(9) M.F. Amr El-Sayed and R.K. Sheline, *J. Inorg. and Nuclear Chem.*, **6**, 187(1958).

(10) K. Haase, and H.M.R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **21**(1), 83(1982).

(11) F. Hibbert and D.P.N. Satchell, *J. Chem. Soc.* (B), 755(1967).

Novel Effects of Polyelectrolytes on Fluorescence Quenching of Tris(2,2'-bipyridine)ruthenium(II) by Methyl Viologen and Cu^{2+}

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The addition of poly(styrenesulfonate) (PSS) to Ru(bpy)$_3^{2+}$ solutions shifted the emission peak by 3 nm to red, and increased emission intensity by 1.8 times. By contrast, poly(vinylsulfonate) (PVS) had little effect on the fluorescence spectrum. The effects of PSS on the spectral properties of Ru(bpy)$_3^{2+}$ were attributed to the presence of a hydrophobic phenyl group in PSS, which interact with Ru(bpy)$_3^{2+}$ by, at least in part, hydrophobic effect. The binding constant of Ru(bpy)$_3^{2+}$ to PSS in 0.1 M NaCl was 6×10^4 M^{-1}, and this value was about 10^3 times higher than those of methyl viologen (MV^{2+}) and Cu^{2+}. The Stern-Volmer constants of emission quenching of Ru(bpy)$_3^{2+}$ by MV^{2+} and Cu^{2+} in 0.1 M NaCl solutions were 426 and 40 M^{-1}, which correspond to second order rate constants(k_q) of 1.1×10^9 and 1.0×10^8 M^{-1}s^{-1}, respectively. The presence of PSS enhanced K_{SV}'s by ∼50 times, whereas PVS increased the values only 1-4 times. The large enhancing effect of PSS, despite of lower charge density than PVS, was explained in terms of longer life-time of photoexcited Ru(bpy)$_3^{2+}$ bound to PSS and strong association of Ru(bpy)$_3^{2+}$ to PSS due to a specific interaction involving hydrophobic effect. The variation of K_{SV}'s on the concentrations of PVS and PSS were also investigated for Ru(bpy)$_3^{2+}$–MV^{2+} and Ru(bpy)$_3^{2+}$–Cu^{2+} photoredox systems.

Introduction

The quenching of the excited triplet state of tris(2,2'-bipyridine)ruthenium(II) cation (Ru(bpy)$_3^{2+}$) via electron transfer reaction has been a subject of intense studies. These studies are mainly focused on the possibility of using the complex cation in conversion of solar energy into the stored chemical energy, and thus, on the enhancement of the efficiency of the conversion.[1] Methyl viologen (MV^{2+}: 1,1'-dimethyl-4,4'-bipyridinium) salts have been most widely used as an electron mediator, *i.e.*, fluorescence quencher. To accelerate the desired electron transfer reaction and/or to prevent back or side reactions, various microheterogeneous systems were extensively utilized.[1,2]

In view of large influences of polyelectrolytes on the rates and yields of many chemical reactions,[2] the effects of polyelectrolytes on the quenching of fluorescence of photoexcited Ru(bpy)$_3^{2+}$ by various quenchers have been investigated.[2-8] Similarly, the electron transfer reactions involving polymer-pendent Ru(bpy)$_3^{2+}$ or viologens were also studied.[9-11] The rates of electon transfer quenching of the excited Ru(bpy)$_3^{2+}$ by Cu^{2+} and Fe^{2+}, for example, were increased up to 3 orders of magnitude by the addition of an anionic polyelectrolyte, poly(vinylsulfonate).[3-5] The remarkable enhancement of the quenching were attributed to the condensation of the Ru(bpy)$_3^{2+}$ and the cationic quenchers in the potential fields of the polyanion by the coulombic interaction.

In this paper, we describe our results of the studies on the fluorescence quenching of Ru(bpy)$_3^{2+}$ by MV^{2+} and Cu^{2+} in poly(styrenesulfonate) (PSS) and poly(vinylsulfonate) (PVS) solutions, which reveal that a specific interaction with polyelectrolytes also greatly affects the rates of the electron transfer reactions between the photoredox couples.

Experimental

Ru(bpy)$_3$(ClO$_4$)$_2$ was prepared by modification of a precedure described in a literature[12] for the preparation of Ru(bpy)$_3$(PF$_3$)$_2$, *i.e.*, the reaction of RuCl$_3$.xH$_2$O and 2,2'-bipyridine was followed by column chromatography on alumina and by precipitation with aqueous NaClO$_4$. PVS and PSS were obtained from Polyscience as sodium salts, and purified by precipitation from ethanol. All solutions were prepared with deionized distilled water. The concentration of Ru(bpy)$_3^{2+}$ was determined by using the value of $\varepsilon_{453} = 14000$ M^{-1}cm^{-1} for the complex ion.[5] The concentrations of polyelectrolytes were