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Photoreactions of *N*-Vinylcarbazole Induced by Metal Salts. VI. Cyclodimerization Catalyzed by Copper(II) Perchlorate in Aprotic Solvents

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Photocyclodimerization of *N*-vinylcarbazole(VCZ) catalyzed by $Cu(ClO_4)_2 \cdot 6H_2O(Cu(II))$ in tetrahydrofuran was investigated under irradiation at 365 nm. At $[Cu(II)]_0 = 10^{-2}$ M in air, when $[VCZ]_0$ was less than 0.4 M, only 1,2-*trans*-dicarbazylcyclobutane(D) was formed, but when $[VCZ]_0$ was higher than 0.5 M, rapid cationic polymerization commenced after about 0.3 M of VCZ had been converted to D. Any consumption of Cu(II) could not be detected in the course of reaction. The change of reaction course from dimerization into polymerization in the midway of reaction was presumably brought about by the consumption of oxygen. Kinetic expression for dimerization rate(R_d) was obtained as follows:

$$R_d \propto I_0^{1.0}[VCZ]_0^{1.0}[Cu(II)]_0^0$$

The quantum yield for D production was much larger than 1, indicating production of D *via* chain mechanism.

A number of metal salts have been found to be effective catalyst for the photosensitized polymerization and cyclodimerization of *N*-vinylcarbazole (VCZ) in organic solution. Sensitizing effect of the group Ib metal salts such as gold(III), silver(I) and copper(II) salts in various aprotic solvents upon these reactions have been preliminarily reported.[1] Due to the subtle changes in the reaction modes, polymerization or cyclodimerization, from system to system and remarkable effects of atmosphere and ligand in some cases, the mechanisms of sensitization by these metal salts seem to be very intricate and to vary with cases. Breitenbach[2] has reported also the photoinduced cyclodimerization in the presence of mercury(II) cyanide, lead(II) thiocyanate or cadmium(II) nitrate in acetonitrile. Ledwith[3] and Wang[4] have investigated the thermal cyclodimerization of VCZ with iron(III) and cerium(IV) in methanolic media to propose two different chain mechanisms involving initiation with the cation radical of VCZ.

The photoreaction of organic substrate in the presence of metal salt can be classified roughly into three categories in terms of the effective light absorption species:

$$\left.\begin{array}{ll} \text{Type I;} & M \xrightarrow{h\nu} M^* \xrightarrow{L} \\ \text{Type II;} & L \xrightarrow{h\nu} L^* \xrightarrow{M} \\ \text{Type III;} & M + L \rightleftarrows ML \xrightarrow{h\nu} \end{array}\right\} \text{reaction products}$$

where M and L denote metal salts and organic substrate, respectively. As described previously,[1] the photodimerization of VCZ catalyzed by copper(II) perchlorate belongs to the Type II analogous to the photopolymerization of VCZ with silver(I) salts.[5] Type II, the reaction of an excited organic molecule with a metal salt, is very unique and has been unequivocally confirmed in a few limited systems.[6] On the other hand, quenching of fluorescence and phosphorescence from excited molecules by metal ions has been studied with emphasis of physical viewpoint.[7] As to photoreactions catalyzed by copper(II) salts, such as cyclodehydrogenation and oxidative fission of stilbene derivatives by copper chloride,[8] methanolysis of styrene by copper(II) perchlorate[9] and chlorination of simple organic substrate by copper(II) chloride[10] examined qualitatively.

In the present article, kinetic and mechanistic studies on the photosensitized cyclodimerization catalyzed by copper(II) perchlorate were undertaken under irradiation of 365 nm light in tetrahydrofuran at 20 °C in air. While effect of solvent, ligand or anion, and atmosphere were examined, cationic polymerization was observed under specific conditions. Furthermore, interaction of the excited VCZ with copper(II) perchlorate as well as with oxygen were investigated quantitatively.

Experimental

N-Vinylcarbazole (Koch-Light Lab. Ltd.) was recrystallized twice from hot *n*-hexane and dried *in vacuo*. $Cu(ClO_4)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ were used after drying *in vacuo* at room temperature. Anhydrous $CuCl_2$ was prepared by drying commercial $CuCl_2 \cdot 2H_2O$ at 110 °C *in vacuo*. $Cu(ClO_4)_2 \cdot 2H_2O$, acetylacetonatocopper(II) and $Cu(ClO_4)_2(pyridine)_4 \cdot 2H_2O$ were prepared.[11] Tetrahydrofuran(THF), ethyl methyl ketone(EMK), ethyl acetate(EA), benzonitrile (BN), acetophenone(AP), and dimethyl sulfoxide (DMSO) were purified by the conventional methods. Purification of all other materials and apparatus for photoreaction were described previously.

Monochromatic light of 365 nm was selected by filtering the emission from a 300 W high pressure Hg lamp with combination of UV-DIA and UV-35 (Toshiba Electric Co. Ltd.) The incident intensity of light was 4×10^{-8} Einstein/min. cm² as determined by the Hatchard-Parker actinometry[12] and controlled with wire meshes. The reaction rate was determined by dilatometry, using a cylindrical quartz cell with parallel flat windows (optical length 10 mm, diameter 44 mm) connected to a capillary with glass joint. No special care was taken to remove dissolved air and trace amount of moisture from the reaction mixture, unless otherwise stated. Pure oxygen or nitrogen was bubbled into the reaction mixtures at least ten minutes prior to reaction if required. To identify 1,2-*trans*-dicarbazylcyclobutane after the comple-

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tion of reaction as confirmed by volume contraction, the reaction mixture was poured into an excess of methanol to precipitate polymer which might be produced simultaneously. After filtration, the filtrate was evaporated to dryness. The residue was confirmed as the cyclodimer from its melting point(195 °C) and its NMR spectra.[13)]

The molecular weight of polymer was determined by viscosity measurement according to the equation, $[\eta]=3.35\times 10^{-4}M^{0.58}$, at 20 °C in benzene.[14)]

Absorption and emission spectra were measured by Shimadzu spectrophotometer MPS-50 and Hitachi fluorescence photometer MPF-3, respectively.

Results

Exploratory experiments were carried out using various kinds of copper(II) species in THF, EMK and DMSO. As shown in Table 1, photo and thermal reactions were dramatically affected by combinations of anion, ligand and solvent. Both hexa- and dihydrate of copper perchlorate gave the same initial rate of photodimerization in THF. Anhydrous copper(II) chloride induced photosensitized cationic polymerization in THF, which was confirmed by additive effects of cationic inhibitors, to produce polyVCZ with molecular weight of about 30000. Meanwhile, acetylacetonato complex and nitrate salt were completely inert in THF. The perchlorate salt seems to be the best catalyst because of its unique reactivity for cyclodimerization indifferent of the kinds of solvent. The reaction modes and the time-conversion curves of the copper perchlorate catalyzed as well as the non-catalyzed photoreactions in a number of solvents under various reaction conditions are depicted in Figs. 1 and 2, respectively, and summarized in Table 2. The behaviors of non-catalyzed photoreaction agreed with the results reported by Mikawa.[15)] Remarkable change in the reaction mode from the non-catalyzed photosensitized radical polymerization to the catalyzed photodimerization in THF and DMSO is particularly interesting. The VCZ–$Cu(ClO_4)_2\cdot 6H_2O$–THF system was chosen for detailed investigation.

Table 1. Effect of anion and ligand

System	THF	EMK	DMSO
$Cu(ClO_4)_2\cdot 6H_2O$	$\mathrm{D^{p}}$	$\mathrm{D^{p}}$	$\mathrm{D^{no}}$
$Cu(ClO_4)_2\cdot 2H_2O$	$\mathrm{D^{no}}$		
$CuCl_2$	$\mathrm{P^{no}}$	$\mathrm{NO^{d>p}}$	
$Cu(NO_3)_2\cdot 3H_2O$	NO	$\mathrm{NO^{d<p}}$	
$Cu(acac)_2$	NO		
$Cu(ClO_4)_2(Py)_4\cdot 2H_2O$	—		$\mathrm{D^{no}}$

$[VCZ]_0=0.25$ M, $[Cu^{II}]_0=10^{-6}-10^{-2}$ M, in air, at 20–25 °C, for 2—3 hr. D,P; photo-dimerization, -polymerization. d,p; thermal dimerization, polymerization. no; no reaction in photosensitized or thermal system. ——; catalyst is insoluble.

Table 2. Reaction products in the absence and presence of $Cu(ClO_4)_2\cdot 6H_2O$ in air

System	No catalyst	$Cu(ClO_4)_2\cdot 6H_2O$
THF	P	D
DMSO	P≫D	D
EMK	D	D
AP	D	D
EA	D	D
BN	D	D

$[VCZ]_0=0.25$ M, $[Cu^{II}]_0=10^{-6}-10^{-2}$ M, $\lambda=365$ nm, P; polymer, D; cyclodimer.

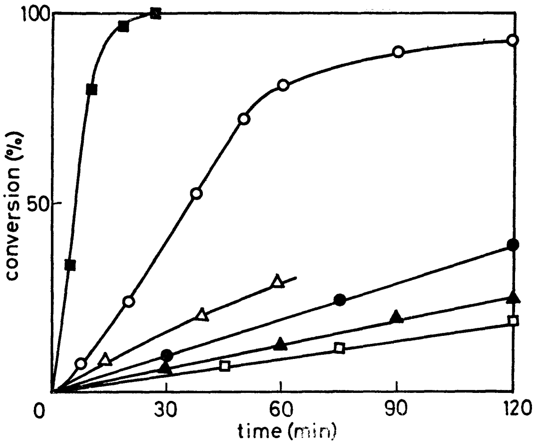

Fig. 1. Effect of solvent on photodimerization of VCZ catalyzed by $Cu(ClO_4)_2\cdot 6H_2O$ in air.
-■-: in BN*1, $[Cu^{II}]_0=10^{-5}$ M, $\lambda=365$ nm, 30 °C.
-○-: in THF, $[Cu^{II}]_0=10^{-2}$ M, $\lambda>365$ nm, 25 °C.
-△-: in AP*2, $[Cu^{II}]_0=10^{-5}$ M, $\lambda=365$ nm, 30 °C.
-●-: in EMK, $[Cu^{II}]_0=10^{-6}$ M, $\lambda=365$ nm, 25 °C.
-▲-: in DMSO, $[Cu^{II}]_0=10^{-2}$ M, $\lambda>365$ nm, 20 °C.
-□-: in EA, $[Cu^{II}]_0=5\times 10^{-6}$ M, $\lambda=365$ nm, 30 °C.
*1 including thermal polymerization.
*2 including photopolymerization without Cu(II).

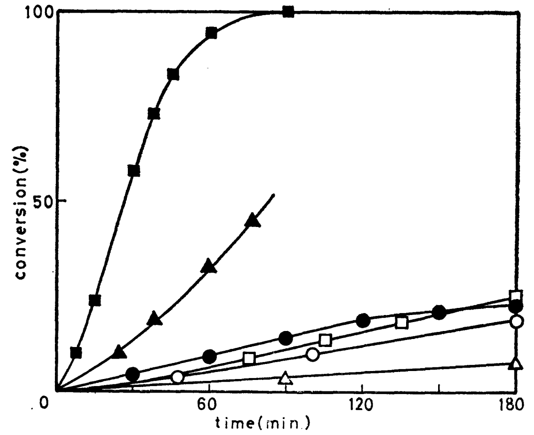

Fig. 2. Effect of solvent on non-catalyzed photoreaction of VCZ in air.
$[VCZ]_0=0.25$ M, 30 °C.
-■-: in BN, $\lambda=365$ nm. -●-: in AP, $\lambda>365$ nm. -□-: in THF, $\lambda>365$ nm. -○-: in EMK, $\lambda=365$ nm. -▲- in DMSO, $\lambda>365$ nm. -△-: in EA, $\lambda=$ 365 nm.

Photoreactions Induced by Copper(II) Perchlorate in THF. Under the standard conditions ($[VCZ]_0=0.25$ M, $[Cu^{II}]_0=10^{-2}$ M, 20 °C, $\lambda=365$ nm, in air), the thermal and non-catalyzed* photoreactions along with photodimerization were negligibly slow.

Light Absorbing Species. Absorption spectra of relevant compounds under the present reaction conditions are shown in Fig. 3. Absorption bands of copper perchlorate appeared in the near ultraviolet region and near infrared region which are assigned to the charge transfer band and the d-d band, respectively. On the other hand, the absorption band of VCZ in the ultraviolet region was scarcely affected by the addition of Cu(II), except negligibly weak 1 : 1 interaction between VCZ and Cu(II). Consequently, the photoenergy at 365 nm was absorbed almost exclusively by VCZ molecule. Meanwhile, it was confirmed that the prolonged irradiation at the d-d band of Cu(II) in longer wavelength region by means of a 500 W incandescent lamp with a cut-off glass filter ($\lambda_{max}=$ 550 nm) induced no photoreaction of VCZ. These facts indicate that the effective absorbing species leading to photoreactions is VCZ itself.

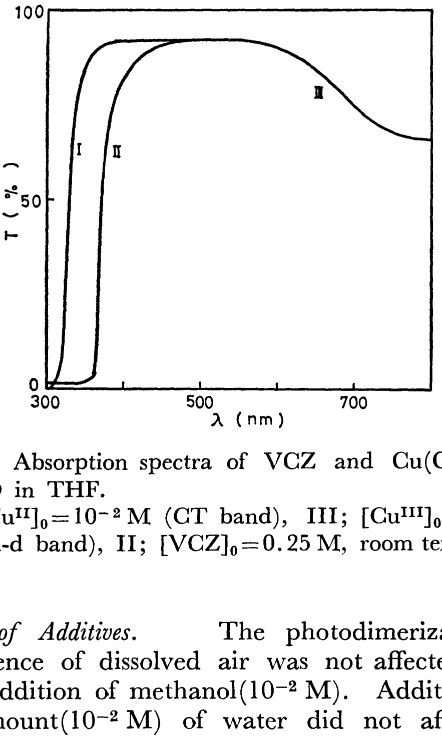

Fig. 3. Absorption spectra of VCZ and $Cu(ClO_4)_2\cdot 6H_2O$ in THF.
I; $[Cu^{II}]_0=10^{-2}$ M (CT band), III; $[Cu^{III}]_0=10^{-2}$ M (d-d band), II; $[VCZ]_0=0.25$ M, room temperature.

Effect of Additives. The photodimerization in the presence of dissolved air was not affected at all by the addition of methanol(10^{-2} M). Addition of a trace amount(10^{-2} M) of water did not affect the initial rate, whereas large amounts of water exceeding 5×10^{-2} M reduced the stationary rate(R_d) as expressed by the following relation.

$$R_d \propto 1/[H_2O]_0$$

Under standard conditions the dimerization proceeded up to the complete conversion after a short acceleration period, while the bubbling of oxygen into reaction mixture prior to irradiation retarded the rate at the early stage of reaction as shown in Fig. 4. When the atmosphere was replaced with nitrogen, remarkably different features of reaction were observed that the rate was accelerated in the midway and polymerization proceeded simultaneously with dimerization. In this case, the fraction of polymer was about 70 percent. This polymerization was of cationic nature as judged by the inhibitory effect of methanol.

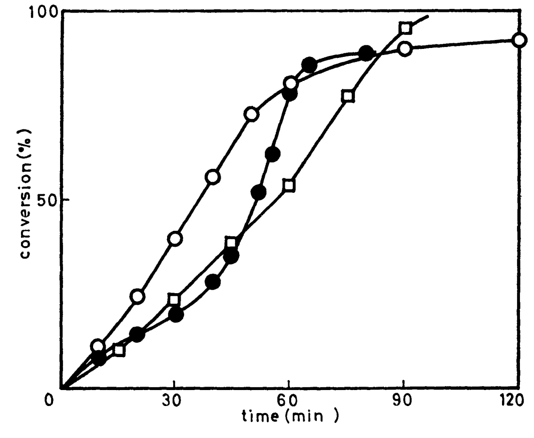

Fig. 4. Effect of atmosphere.
$[VCZ]_0=0.25$ M, $[Cu^{II}]_0=10^{-2}$ M, 25 °C.
-○-: in air. -□-: in oxygen. -●-: in nitrogen.

Effect of Monomer Concentration. At $[Cu^{II}]_0=$ 10^{-2} M in air, when $[VCZ]_0$ was less than approximately 0.4 M, cyclodimer was formed. When $[VCZ]_0$ was higher approximately 0.5 M, the authors have found an unusual phenomenon that rapid polymerization commenced after the conversion of 0.25—0.3 M of VCZ to the cyclodimer, as demonstrated in Fig. 5. This polymerization was inhibited by methanol(5×10^{-2} M) but not by DPPH (2×10^{-4} M), indicating cationic polymerization. On the other hand, when the reaction system was saturated with oxygen

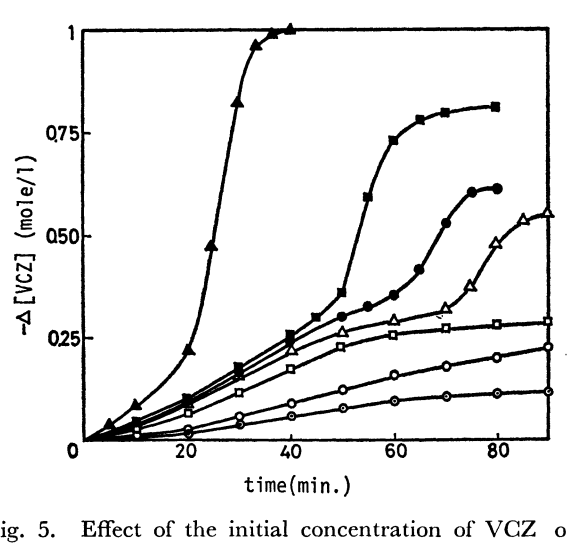

Fig. 5. Effect of the initial concentration of VCZ on the photoreaction.
$[Cu^{II}]_0=10^{-2}$ M, 20 °C, in air.
$[VCZ]_0$(M): -⊙-: 0.125. -○-: 0.25. -□-: 0.40. -△-: 0.50. -●-: 0.60. -■-: 0.75. -▲-: 1.0.

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* This photopolymerization was completely inhibited by 1,1-diphenyl-2-picrylhydrazyl(10^{-4} M) but not affected by methanol (10^{-2} M), indicating radical propagation. Since the rate of polymerization(R_p) *in vacuo* was less than a half of that in the presence of dissolved air, oxygen seems to participate more or less in the initiation processes. The R_p was expressed as follows:

$$R_p \propto I_0^{0.45}[VCZ]_0^{1.4}$$

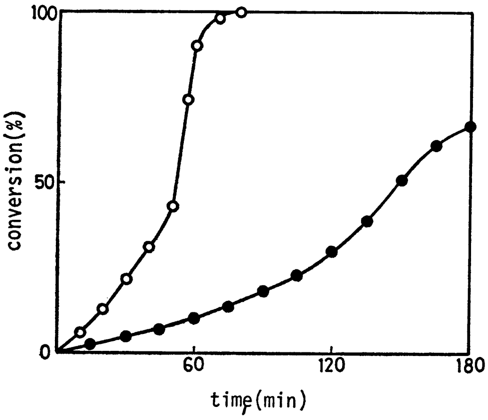


Fig. 6. Effect of an excess of oxygen.
$[VCZ]_0 = 0.75$ M, $[Cu^{II}]_0 = 10^{-2}$ M, 20 °C.
-○-: in air. -●-: in saturated oxygen.

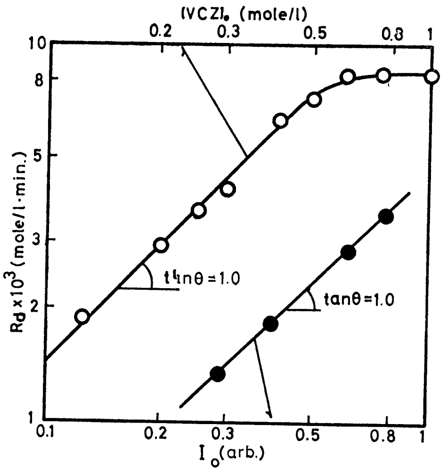


Fig. 7. Dependence of R_d on $[VCZ]_0$ and I_0.
$[Cu^{II}]_0 = 10^{-2}$ M, 20 °C, in air.
-○-: $[VCZ]_0$ = variable, I_0 = constant.
-●-: $[VCZ]_0 = 0.25$ M, I_0 = variable.

before photoirradiation, the cationic polymerization in the later stage was suppressed, and the cyclodimer alone was obtained all through the reaction with a slower rate, as shown in Fig. 6. This fact suggests that oxygen plays some major roles in either the production of the cyclodimer or the inhibition of the polymer formation, and that the subsequent polymerization starts after the consumption of oxygen.

Dependence of the stationary rate (R_d) after the short acceleration period on the initial concentration of VCZ is shown in Fig. 7. Although R_d saturated at higher concentration, R_d was proportional to $[VCZ]_0$ up to 0.5 M VCZ.

Effects of Copper(II) Perchlorate Concentration. In the concentration range of 10^{-3}—10^{-1} M of copper perchlorate the initial R_d is nearly constant. The saturation of time conversion curve was observed at lower conversion with increasing $[Cu^{II}]_0$. This saturation effect seems to be attributed to the different concentration of water involved in these Cu(II) salts, since the same effect was observed when water was added into the reaction mixture. Another finding in support of this assumption is the fact that the dimerization by dihydrate copper(II) perchlorate proceeded up to nearly the complete conversion without saturation.

Changes of $[Cu^{II}]$ during the reaction were measured spectroscopically by following the d-d absorption band of Cu(II). Any consumption of Cu(II) could not be detected in the course of both dimerization ($[VCZ]_0 =$ 0.25 M) and polymerization($[VCZ]_0 = 0.75$ M) subsequent to dimerization, indicating the role of Cu(II) to be purely catalytic.

Quantum Yield for Dimer Production. Linear dependence of R_d on the incident intensity of light(I_0) was depicted in Fig. 7. Upon interrupting irradiation, the dimerization stopped completely after a short after-effect, as shown in Fig. 8, indicating the production of relatively short lived species. The apparent quantum yield for dimer production including the after-effect was calculated from Fig. 8 to be about 15. This value of more than unity suggests that the cyclodimer is formed *via* some type of chain mechanism.

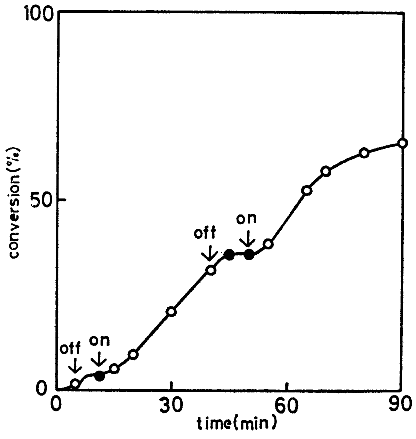


Fig. 8. On-off test.
$[VCZ]_0 = 0.25$ M, $[Cu^{II}]_0 = 10^{-2}$ M, 20 °C, in air.

Interaction of the Excited Singlet State of VCZ with Copper(II) Perchlorate or Oxygen. As shown in Table 3, under excitation at 345 nm VCZ emitted monomer and excimer fluorescence at 365—370 nm and at 460 nm, respectively. The mirror image relation of absorption and monomer emission spectra was held very well. Excimer fluorescence was observed only at high concentration of VCZ. Both fluorescences were quenched by Cu(II), where the Stern-Volmer plots fall on a straight line as typically depicted in Fig. 9. The quenching constants $K_{q,Cu}(=k_{q,Cu}\cdot\tau_0)$ for monomer and excimer emission were exactly identical as shown in the first row in Table 3. On the other hand, oxygen also quenched both emissions to nearly an equal extent(the second row). Therefore, $K_{q,Cu}$ must depend on the concentration of oxygen. Assuming the concentration of dissolved oxygen as 10^{-3} M and conformity to the Stern-Volmer equation as well, K_{q,O_2} was calculated from measurements of emission in air, nitrogen and oxygen in the presence of an appropriate concentration of Cu(II). Dependence of atmosphere on $K_{q,Cu}$ was also tabulated in Table 3 (the third row). The value of K_{q,O_2} (the forth row) thus

Table 3. Quenching constants

[VCZ] (M)	Atmosphere or $[Cu^{II}]_0$	λ_{ex} (nm)	λ_{em} (nm)	$K_{q,Cu}$	K_{q,O_2}
10^{-1}	in air	345	370	206	—
	in air	345	460	206[a]	—
	$[Cu^{II}]_0 = 0$ M	345	370	—	500
	$[Cu^{II}]_0 = 0$ M	345	460	—	680[a]
	$[Cu^{II}]_0 = 10^{-2}$ M	345	370	—	190
10^{-4}	in N_2	345	365	119	—
	in air	345	365	84	—
	in O_2	345	365	55	—
	$[Cu^{II}]_0 = 0$ M	345	365	—	590
	$[Cu^{II}]_0 = 10^{-2}$ M	345	365	—	430
	$[Cu^{II}]_0 = 5 \times 10^{-2}$ M	345	365	—	180
	$[Cu^{II}]_0 = 10^{-1}$ M	345	365	—	80

a) For excimer emission

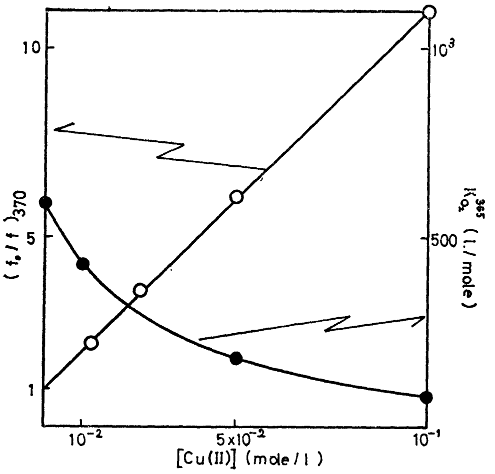


Fig. 9. The Stern-Volmer plot and K_{q,O_2} as a function of $[Cu^{II}]_0$.
-○-: $[VCZ]_0 = 0.1$ M, $\lambda_{ex} = 365$ nm, in air.
-●-: $[VCZ]_0 = 10^{-4}$ M, $\lambda_{ex} = 345$ nm.

calculated was depicted as a function of $[Cu^{II}]$ in Fig. 9.

Discussion

Photoreactions of VCZ in the presence of copper(II) salts exhibited very intricate features depending on various factors such as anion or ligand of the salt, solvent, atmosphere, water or concentration of VCZ. The fact that copper perchlorate induces the photocyclodimerization alone indifferent of solvent under the condition of $[VCZ]_0 = 0.25$ M and in the presence of air is the characteristic nature of this metal salt in contrast to gold(III) complexes or silver(I) salts.[1] The authors classified[1] the photoreactions of VCZ with these metal salts into three categories in terms of the effective light absorbing species: Type I; metal salt, Type II; VCZ and Type III; VCZ/metal salt complex. The copper perchlorate-THF-365 nm system belongs to the Type II similar to the photoreaction with silver(I) salts. In the latter system, however, cyclodimerization and/or cationic polymerization took place depending upon solvents.

The sequences of the rate of photocyclodimerization in both Cu(II) catalyzed and non-catalyzed systems seem to depend upon the donor-number of solvent (DN) proposed by Gutmann,[16] which is an indication of donating power of solvent to cation, as follows:

$Cu(ClO_4)_2 \cdot 6H_2O$ system:

R_d; BN>EMK∼AP>EA>THF>DMSO

DN; 12< <17< 20 < 30

Non-catalyzed system: R_d; BN≫EMK≳AP>EA

The parallelism between the Cu(II) catalyzed and non-catalyzed photoreactions with respect to the solvent effect on R_d suggests that the major solvent effect is not to influence the activity of Cu(II). The cyclodimerization in DMSO in the presence of Cu(II) should be noted since such reaction has not been reported in the cases of photo- or γ-ray induced reactions both in the presence and absence of organic acceptors.

Effect of atmosphere on the reaction mode is of interest. When $[VCZ]_0$ is higher than 0.5 M, the rapid cationic polymerization commences after about 0.3 M of VCZ has been converted to the cyclodimer and in the presence of an excess of oxygen this polymerization is completely suppressed and cyclodimerizaiton alone proceeds. These findings suggest that oxygen is indispensable to the formation of cylcodimer or for the inhibition of cationic polymerization, and that oxygen is consumed in the course of the cyclodimerization. This oxygen effect is also supported by the fact that cationic polymerization predominates in nitrogen atmosphere.

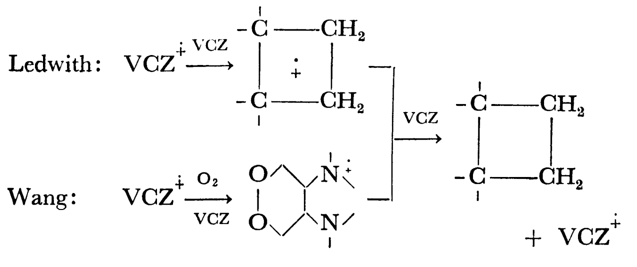
Kinetic relation, $R_d \infty I_0[VCZ]_0\ [Cu^{II}]_0^0$, is identical with that of the photodimerization by $Hg(CN)_2$ in acetonitrile briefly described by Breitenbach.[2] Apparent quantum yield for the production of cyclodimer is observed to be about 15, suggesting the chain mechanism as proposed by Ledwith in the photocyclodimerization sensitized by organic dyes.[3]

Fluorescence of VCZ was quenched by both Cu(II) and oxygen. Provided that the actions of Cu(II) and oxygen on fluorescence are mutually independent, the following equations are derived, respectively.

$$K_{q,O_2} = \frac{K^\circ_{q,O_2}}{1+K^\circ_{q,Cu}[Cu^{II}]}, \quad K_{q,Cu} = \frac{K^\circ_{q,Cu}}{1+K^\circ_{p,O_2}[O_2]}$$

where, K°_{q,O_2} and $K^\circ_{q,Cu}$ denote the intrinsic quenching constants of oxygen and Cu(II) in the absence of the other, respectively. These hyperbolic relations agree with the experimental results qualitatively. Fluorescence of VCZ is supposed to be quenched dynamically by Cu(II), since interaction between VCZ and Cu(II) in the ground state is negligible. Meanwhile, dynamic quenching by oxygen may not be characterized unequivocally because of possible formation of the ground state charge-transfer complex. The equal quenching constants for monomer and excimer emissions indicate that apparent quenching of excimer emission was attributed to a result of quenching of monomer fluoressence. Quantitative studies on the quenching of organic fluorescence by metal ion have been scarcely reported.[7] On the other hand, the quenching effect of inorganic ion on phosphorescence has been investigated systematically by several authors to some extent.[7] Although in the present study no phosphorescence was observed under reaction conditions, at room temperature and in air, interactions of the excited triplet state of VCZ with Cu(II) ion seem to be also very likely, as inferred from quenching action of Cu(II) to the triplet state of aromatic molecules.[7] Quenching mechanisms may be roughly classified into three categories: i) energy-transfer ii) electron-transfer iii) enhancement of intersystem crossing $S^* \rightarrow T^*$. Similar quenching action of oxygen to the excited aromatic molecule has been reported in details.[17]

As to the mechanism of cyclodimerization of VCZ, the following different two types of mechanisms have been proposed by Ledwith[3] and by Wang,[4] respectively.

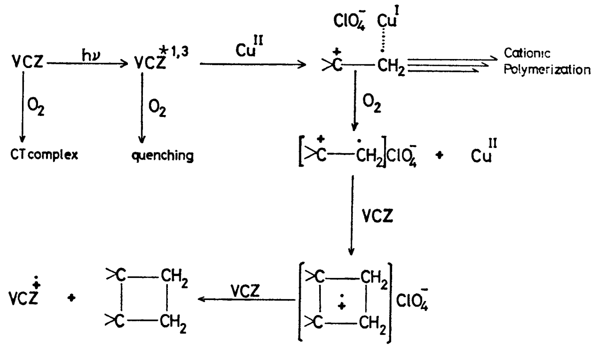


Both mechanisms are common in the sense of assuming chain reaction *via* radical-cation intermediate ($M^{\dot{+}}$). The former assumed the cyclodimer radical cation intermediate ($D^{\dot{+}}$) whereas the latter considered the six-membered ring peroxide intermediate. However, the problem of oxygen consumption has never been investigated by them. Recently, the direct evidence for the following equilibrium

$$M^{\dot{+}} + VCZ \rightleftarrows D^{\dot{+}}$$

was obtained by means of the pulse radiolysis technique by Imamura.[18] They have proposed that $D^{\dot{+}}$ is a common precursor for both cyclodimerization and cationic polymerization of VCZ.

The following reaction scheme is proposed. Either excited singlet or triplet state ($VCZ^{*1,3}$) would collide with Cu(II), while one electron transfer from $VCZ^{*1,3}$ to Cu(II) produces $VCZ^{\dot{+}}$ and Cu^{I}. Simultaneously, Cu^{I} would interact with radical part of the $VCZ^{\dot{+}}$ in either the formation of organometallic bond or radical complex[19] to stabilize the free spin and consequently, cationic polymerization is initiated from the carbonium ion. The role of oxygen is to oxidize Cu^{I} to Cu^{II} accompanied by the production of radical-anion of oxygen ($O_2^{\dot{-}}$) and the free $VCZ^{\dot{+}}$ which reacts with VCZ to produce the cyclodimer cation-radical ($D^{\dot{+}}$). Subsequent processes would be almost similar to the Ledwith's chain mechanism with the exception of the role of $O_2^{\dot{-}}$ and termination reaction. In this mechanism, propagation proceeds *via* $D^{\dot{+}}$ with a counter-ion $O_2^{\dot{-}}$ and termination takes place by electron-transfer between them resulting none of consumption of molecular oxygen. In the present study, however, it is suggested that oxygen is consumed through the main route of the reaction but not as side reactions, since about 0.3 M VCZ was always converted into the cyclodimer indifferent of the initial concentration of VCZ if it is over 0.4 M, as shown in Fig. 5, under the standard conditions. Therefore, $O_2^{\dot{-}}$ might be consumed by some types of bimolecular reaction as reported in the pulse radiolysis studies[20] or the cerium(IV) salt catalyzed reaction of hydroperoxide.[21]



Scheme

Termination is assumed as monomer termination, for example, the Friedel-Crafts type reaction of carbonium ion with the carbazyl ring as proposed previously.[22] By applying the assumption of stationary concentration $M^{\dot{+}}$, $D^{\dot{+}}$ and $>\overset{+}{C}-\dot{C}\cdots\cdots Cu^{I}$, the following rate expression is derived.

$$R_d \propto I_{abs}^{M}[Cu^{II}]_0{}^0 = I_0\{1-\exp(-\varepsilon_M[VCZ]_0)\}\ [Cu^{II}]_0{}^0$$

This kinetic relation explains the experimental results very well. Another role of oxygen in this mechanism is the interaction with either ground state or excited state of VCZ to quench the emission of VCZ, which may result the retardation of the rate in the presence of an excess of oxygen in the reaction system. Further detailed investigations on the vacuum system and the direct measurement of oxygen consumption as well as the effects of water would be future problems.

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