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The Photoreduction Mechanism of 10-Methylacridinium Chloride in Methanol. The Formation of 9,10-Dihydro-9-methoxy-10-methylacridine and Hydride Transfer

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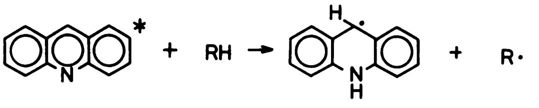
The photolysis of 9,10-dihydro-9-methoxy-10-methylacridine (MeOA), which is a product of the nucleophilic addition of methanol to 10-methylacridinium chloride, yielded 9,10-dihydro-10-methylacridine (AH_2) and 10,10′-dimethyl-9,9′,10,10′-tetrahydro-9,9′-biacridinyl ($(AH)_2$) in various solvents. The quenching experiment using 1,3-pentadiene indicates that AH_2 and $(AH)_2$ are produced from the photoexcited singlet and triplet states of MeOA respectively. The results on the solvent effects and the photolyses in solvent matrices at 77 K suggest that the photochemical reaction of MeOA yielding AH_2 occurs via hydride transfer from the methoxide anion to the 10-methylacridinium cation, these ions being generated from the heterolysis of MeOA in the photoexcited singlet state.

The photochemical reduction of acridine in alcohols has been a well-studied subject.[1—15] 9,10-Dihydroacridine is a major photoproduct of the dilute alcoholic solutions of acridine ($<10^{-3}$ M, 1 M=1 mol dm^{-3}), while 9,9′,10,10′-tetrahydro-9,9′-biacridinyl is also produced at higher acridine concentrations ($<10^{-1}$ M).[2] Photoexcited acridine (n, π* singlet or triplet states) abstracts a hydrogen atom from a solvent to yield the 9,10-dihydroacridinyl radical, which subsequently gives 9,10-dihydroacridine and 9,9′,10,10′-tetrahydro-9,9′-biacridinyl through disproportionation and coupling reactions respectively (Eqs. 1—3).[16] The photochemical reactions of the 10-methylacridinium ion (A^+) in alcohols are somewhat similar to those of acridine.[2,3,6,17] For example, the photolysis of 1.2×10^{-3} M 10-methylacridinium chloride (A^+Cl^-) in methanol containing trimethylamine gives 9,10-dihydro-10-methylacridine (AH_2) and 9,10-dihydro-9-hydroxymethyl-10-methylacridine in 11 and 28% yields respectively.[6] At higher concentration of A^+Cl^- (2.2×10^{-2} M) in ethanol, 10,10′-dimethyl-9,9′10,10′-tetrahydro-9,9′-biacridinyl ($(AH)_2$, 17%) is formed, together with AH_2 (12.7%) and 9,10-dihydro-9-(1-hydroxyethyl)-10-methylacridine (12.6%). Although the photoreduction mechanism of acridine has been studied in detail,[16] that for the acridinium ion is still unresolved. Zanker et al. have postulated a mechanism for the formation of $(AH)_2$ involving hydrogen abstraction by the photoexcited acridinium ion from ethanol.[17] Such hydrogen abstraction by the photoexcited acridinium ion, however, is hard to accept because the 10-alkylacridinium ion has no odd electrons which can participate in the n–π* transition.



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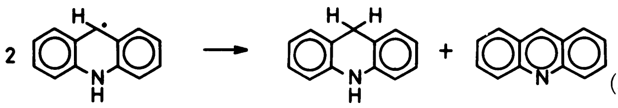

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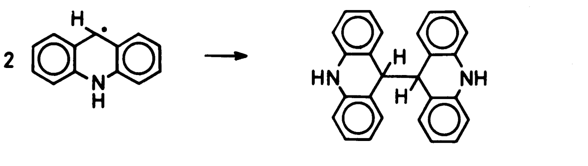
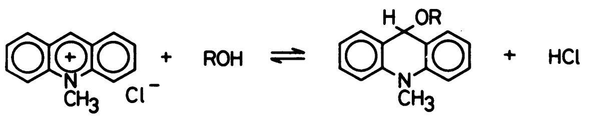


(3)

In the present paper, we demonstrate a mechanism of the photoreduction of A^+Cl^- in a methanolic solution which is quite different from those for acridine. In a previous communication, we reported a nucleophilic addition of primary and secondary alcohols to the 9-position of A^+Cl^- in dilute solutions ($[A^+Cl^-]=1\times10^{-5}$ M):[18]



(4)

The mechanisms presented herein involve the photoreactions of 9-methoxy-9,10-dihydro-10-methylacridine, a methanol adduct of A^+Cl^-.

Experimental

A^+Cl^- was prepared by passing an aqueous solution of 10-methylacridinium iodide through an ion-exchange column (Dowex-1- X8), the crude A^+Cl^- thus obtained was recrystallized from acetonitrile. 9,10-Dihydro-9-methoxy-10-methylacridine (MeOA),[19] AH_2,[20] and $(AH)_2$[6] were prepared according to the procedures described in the literature. 1,3-Pentadiene was distilled. The analysis by means of HPLC indicated that distilled 1,3-pentadiene was still a mixture of cis and trans isomers. Spectral grades of methanol, ethanol, and 2-propanol were refluxed in the presence of K_2CO_3 and distilled. The other solvents (reagent grades) were used without further purification. All the solvents were dried using molecular sieves. Water was distilled and passed through an ion-exchange column.

The absorption spectra were taken on a Shimadzu UV-200S spectrophotometer. The fluorescence and phosphorescence spectra were measured by means of a Hitachi 650-60 spectrofluorometer. Photolyses were carried out by using an Ushio USH-5000 super-high-pressure Hg lamp (500 W) as the point-light source. The sample, in a Pyrex tube (ϕ=4 mm) or in a quartz cell (1-cm optical length), was placed at a distance of 60 cm from the light source. The deaeration of the sample was performed by five freeze-pump-thaw cycles. For photolyses and/or spectroscopic measurements at 77 K, the sample in the glass tube was placed in a Dewar vessel equipped with a quartz cell. The identification and the quantitative analyses of photoproducts were performed by a Shimadzu LC-5A HPLC apparatus equipped with a column of Shimadzu ZORBAX ODS (46×250 mm). AH_2, $(AH)_2$, and 10-methyl-9(10*H*)-acridinone (A=O) could be analyzed by means of HPLC but not A^+Cl^- and MeOA.

Results and Discussion

Nucleophilic Addition of Alcohols to A^+Cl^-. The absorption spectra of A^+Cl^- in water and alcohols are shown in Figs. 1 and 2. The assignments of the absorption bands of acridinium compounds blended in polymer films have been done by linearly-polarized absorption spectroscopy.[21,22] The shape of the absorption spectrum of A^+Cl^- (1×10^{-5} M) in water (pH 5.5) is essentially the same as that in polymer film. As is shown in Fig. 1, however, the spectrum in methanol is completely different from that in water; i.e., the ^1L_a (440, 415, and 395 nm), ^1L_b (358 and 343 nm) and ^1B_b (258 and 242 nm) bands observed in water disappear in methanol, while new absorption bands appear at 320 and 280 nm. This spectral change of A^+Cl^- in methanol has been ascribed to the formation of MeOA, which is a product of the nucleophilic addition of methanol to A^+Cl^- (Eq. 1).[18] MeOA was not formed in methanol containing small amounts of HCl. Figure 3 shows the absorption spectra of various concentrations of A^+Cl^- in methanol. An increase in the initial concentration of A^+Cl^- causes a decrease in the conversion of A^+Cl^- into MeOA. The addition of triethylamine to the system, containing both MeOA and A^+Cl^-, caused the disappearance of A^+Cl^- and an enhancement of the MeOA formation. These results clearly indicate the equilibrium shown in Eq. 4. Although it is expected that the equilibrium constant (*K*) can be determined spectroscopically, the poor reproducibility did not allow us to get an accurate *K* value. The determination of *K* is now in progress.

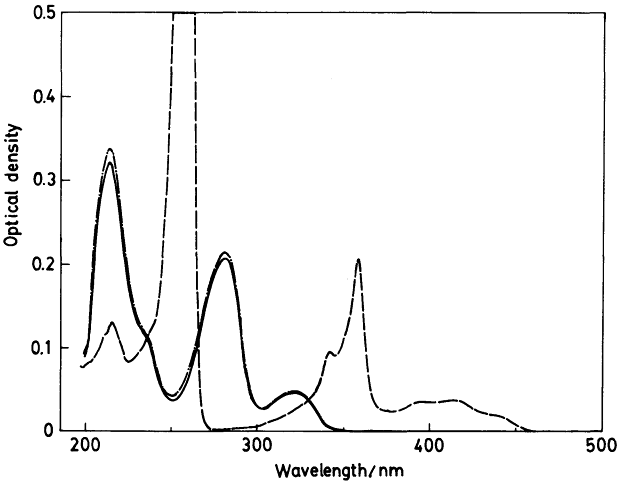


Fig. 1. Absorption spectra of A^+Cl^- (1×10^{-5} M) in water (----) and methanol (——) and authentic MeOA (1×10^{-5} M) in methanol (—·—) at 25 °C.

As is shown in Fig. 2, ethanol also converts A^+Cl^- to 9,10-dihydro-9-ethoxy-10-methylacridine. The nucleophilic addition of primary alcohols to A^+Cl^- occurs in 1-propanol, 1-butanol, and 1-octanol, but not in grycerol. *t*-Butyl alcohol does not give an alcohol adduct (Fig. 2). In the case of a secondary alcohol, 2-propanol, small amounts of unreacted A^+Cl^- coexist with the corresponding 9-alkoxy-9,10-

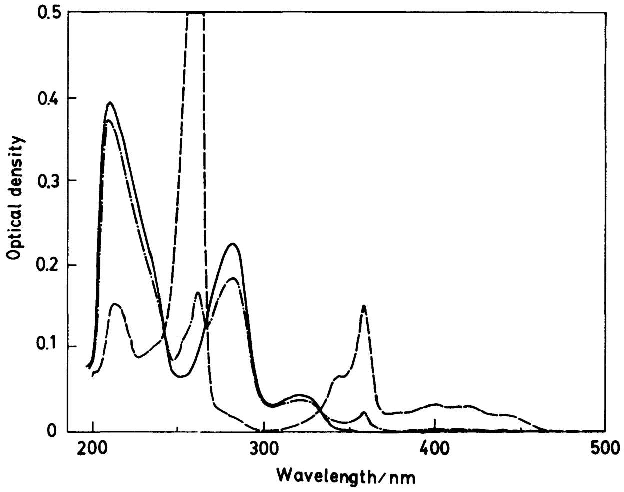


Fig. 2. Absorption spectra of A^+Cl^- (1×10^{-5} M) in ethanol (——), 2-propanol (—·—), and *t*-butyl alcohol (----) at 25 °C.

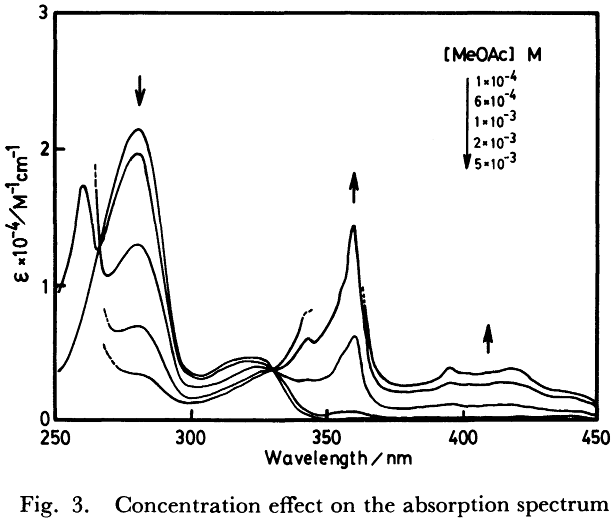


Fig. 3. Concentration effect on the absorption spectrum of A^+Cl^- in methanol at 25 °C.

dihydro-10-methylacridine. These findings reveal that the formation of 9-alkoxy-9,10-dihydro-10-methylacridine is sensitively affected by steric factor(s). Steric hindrance due to the hydrogen atoms at the 1- and 8-positions of the acridinium ring and the thermodynamically unstable structures of the alcohol adducts may inhibit the formation of 9-alkoxy-9,10-dihydro-10-methylacridines in 2-propanol, *t*-butyl alcohol, and glycerol.

It has been known that the 9-position of the 10-methylacridinuim ion (A^+) is so electrophilic that such nucleophiles as hydroxide[20,23—27] and methoxide anions[19,28,29] attack this position, thus yielding 9-hydroxy- and 9-methoxy-9,10-dihydro-10-methylacridines respectively. Our present observation reveals that weaker nucleophiles, the alcohols, also attack the 9-position of A^+. A^+Cl^- acts as a pseudo acid in the primary and secondary alcohols, such as methanol, ethanol, 1-propanol, 1-butanol, 1-octanol, and 2-propanol (Eq. 4).

Photolysis of MeOA. It is reasonable to assume that the primary step in the photoreaction of a dilute methanolic solution of A^+Cl^- is the photoexcitation of MeOA. Therefore, we studied the photochemical reaction of MeOA under various conditions.

Figure 4 shows the progressive absorption spectral changes of MeOA (5×10^{-5} M) in deaerated ethanol upon irradiation at room temperature. The photolyzed solution was analyzed by means of HPLC. $(AH)_2$ was produced as a major photoproduct, along with small amounts of AH_2 and A=O. $(AH)_2$ was isolated from the photolyzed solution of MeOA (5×10^{-4} M) and identified by means of ^{1}H NMR and elementary analysis. The results of the fluorescence spectral measurment of the photolyzed solution (λ_{ex}=298 nm) support the formation of AH_2 (λ_{em}=360 nm).

The yields of AH_2, $(AH)_2$ and A=O for the photolyses of MeOA in methanol, ethanol, 2-propanol, and acetonitrile under anaerobic and aerobic conditions are summarized in Table 1. Under anaerobic conditions, AH_2, $(AH)_2$, and A=O are formed, and the yields of $(AH)_2$ are higher than those of AH_2 in all the solvents used herein. In air-saturated solutions, however, the formation of $(AH)_2$ was almost completely depressed, and the yields of AH_2 increased remarkably. Prolonged irradiation in aerated solvents, especially in 2-propanol, led to an enhancement of the A=O formation (Fig. 5). In 2-propanol, the rapid formation of AH_2 was followed by the decomposition of AH_2, while the yield of A=O gradually increased. The reaction profile for the photolysis in acetonitrile

Table 1. Photochemical Reactions of MeOA in Deaerated and Aerated Solvents[a)]

Solvent	Yield/%[b)]		
	A=O	AH_2	$(AH)_2$
Methanol	6 (1)	14 (32)	19 (0)
Ethanol	4 (5)	7 (35)	40 (0)
2-Propanol	2 (31)	5 (20)	19 (1)
Acetonitrile	3 (21)	5 (21)	24 (0)

a) MeOA (5×10^{-5} M) in a solvent was irradiated with a 500 W super-high pressure Hg lamp for 2 min at room temperature. The yields of the photoproducts were determined by means of HPLC. b) The values in parentheses are the yields for the photolyses in air-saturated solvents.

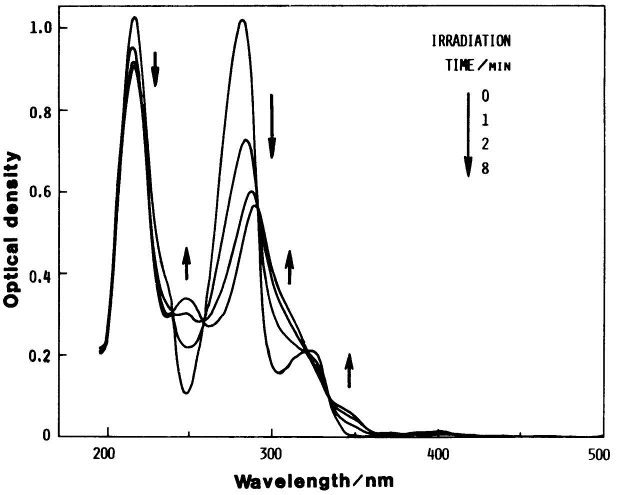


Fig. 4. Progressive absorption spectral changes of MeOA (5×10^{-5} M) in deaerated ethanol upon full irradiation with a 500 W super-high pressure Hg lamp at room temperature.

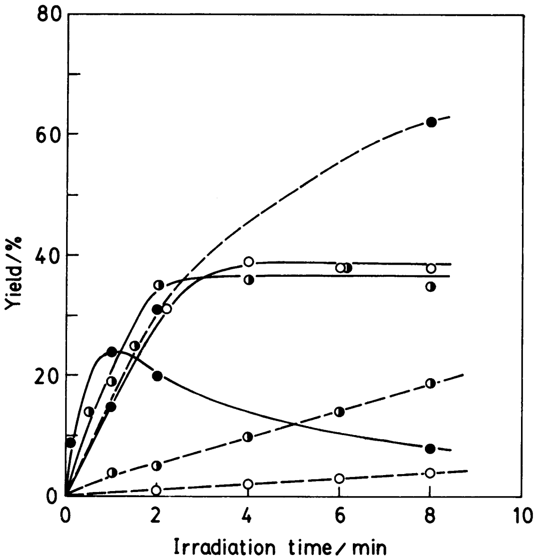


Fig. 5. Plots of the yields of AH_2 (——) and A=O (----) against the irradiation time when MeOA (5×10^{-5} M) in air-saturated methanol (○), ethanol (◑), and 2-propanol (●) was irradiated with a 500 W super-high pressure Hg lamp at room temperature.

was similar to that in 2-propanol (the data are not shown). In the cases of methanol and ethanol, the formation of A=O continued even after the rate of the AH_2 formation has become a plateau. These findings suggest that A=O is formed by the photooxidation of AH_2. Figure 6 shows the progressive absorption-spectral changes, which show the time course of the photoreaction of AH_2 (5×10^{-5} M) in air-saturated acetonitrile. The isosbestic points were observed at 325, 276, and 216 nm. The spectrum of the final photoproduct is completely in agreement with that of authentic A=O. Rapid photooxidation giving A=O was also found for $(AH)_2$ in aerated acetonitrile and 2-propanol (Fig. 7). It can be concluded, therefore, that A=O is produced by the photooxidation of AH_2 and/or $(AH)_2$ in these solvents. In methanol and ethanol, however, there was a very slow photooxidation of AH_2. A 70-min irradiation in methanol gave A=O in only a 30% yield. The reaction profiles for the photolyses of MeOA in methanol and ethanol shown in Fig. 5 can be explained by saying that the rate of AH_2 formation competes with that of the photooxidation of AH_2 to A=O at a longer irradiation time. The photolysis of $(AH)_2$ in methanol did not produce A=O at an initial stage, but a photoproduct with an absorption maximum at 280 nm was formed upon irradiation for 1 min. The HPLC analysis indicated the photoproduct to be AH_2 (40% yield). Under anaerobic conditions, however, no photoinduced conversion of $(AH)_2$ to AH_2 occurred. At the present stage, the solvent effects on the photooxidation of AH_2 and $(AH)_2$ and the effects of oxygen on the photoreaction of $(AH)_2$ are not understood.

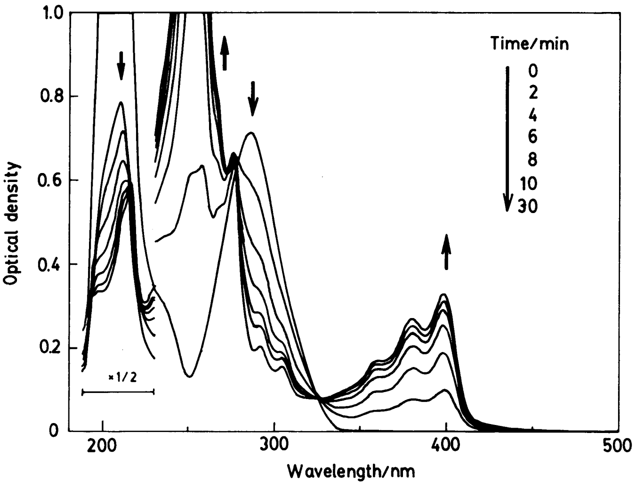


Fig. 6. Progressive absorption spectral changes of AH_2 (5×10^{-5} M) in air-saturated acetonitrile upon irradiation with a 500 W super-high pressure Hg lamp at room temperature.

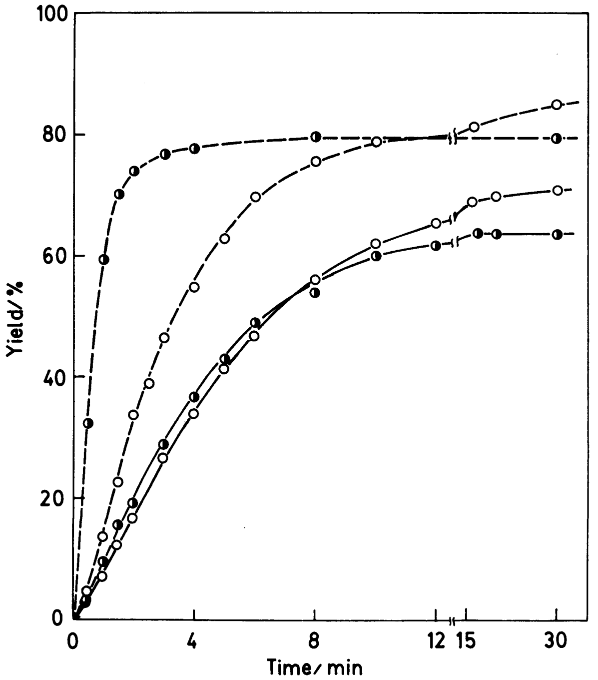


Fig. 7. Plots of the yields of A=O against the irradiation time when AH_2 (——) and $(AH)_2$ (----) in air-saturated 2-propanol (○) and acetonitrile (◐) were irradiated with a 500 W super-high pressure Hg lamp at room temperature.

Effects of 1,3-Pentadiene. The photochemical reaction of MeOA is very sensitive toward oxygen dissolving in solutions (vide supra). Oxygen can be expected to be a triplet-quencher for the photoreactions of MeOA. The photochemical reactions of MeOA under aerobic conditions, however, were so complex that the role of oxygen as a triplet quencher

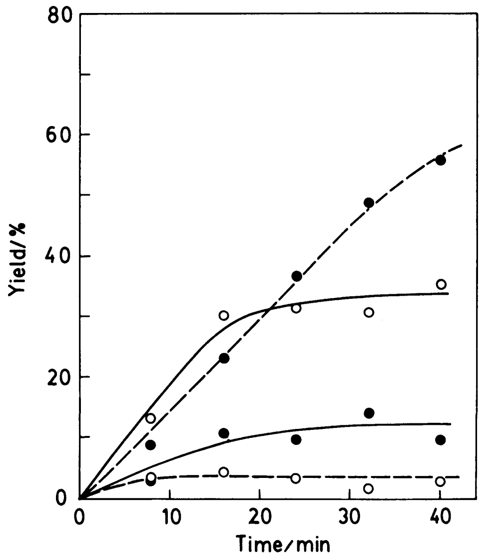


Fig. 8. Plots of the yields of AH_2 (○) and $(AH)_2$ (●) against the irradiation time when MeOA (5×10^{-5} M) in deaerated ethanol was irradiated with a 500 W super high-pressure Hg lamp (> 300 nm) in the absence (----) and the presence (——) of 1,3-pentadiene (1×10^{-2} M) at room temperature.

could not be verified from the results presented above. Therefore, we examined the photolysis of MeOA (5×10^{-5} M) in degassed ethanol containing 1,3-pentadiene, which is well-known as an effective triplet quencher.[30]

The effects of 1,3-pentadiene (1×10^{-2} M) on the yields of AH_2 and $(AH)_2$ are shown in Fig. 8. The samples were irradiated by light with wavelengths above 300 nm (glass filter) in order to avoid the excitation of the 1,3-pentadiene. As Fig. 8 clearly shows, 1,3-pentadiene inhibited the formation of $(AH)_2$ and enhanced the yield of AH_2. The effects of 1,3-pentadiene are similar to those of oxygen. $(AH)_2$ did not decompose at all upon irradiation (>300 nm). Judging from these results, it can be concluded that AH_2 and $(AH)_2$ are produced via the lowest excited singlet and triplet states of MeOA respectively.

Photolyses of MeOA in Rigid Matrices and Reaction Mechanisms. In order to detect the reaction intermediate(s) for the photoreaction of MeOA, MeOA (5×10^{-5} M) in ethanol was irradiated at 77 K. In a glassy ethanol matrix, MeOA showed an absorption spectrum similar to that in the liquid phase except for the bands at around 320 nm, a broad absorption band at 320 nm in the fluid medium being split into two bands in the ethanol matrix (Fig. 9). Photoirradiation caused a rapid disappearance of the absorption bands of MeOA and the appearance of the characteristic absorption bands attributable to the 10-methylacridinium cation (A^+) (Fig. 9). The photoproduct should be 10-methylacridinium methoxide (A^+MeO^-). The emission spectra of the photolyzed solution were also measured (Fig. 10). Although MeOA does not fluoresce in ethanol at room temperature, it emits fluorescence with a maximum intensity at 337 nm (λ_{ex}=288 nm) in glassy ethanol at 77 K. Upon irradiation, the fluorescence intensity due to MeOA decreased, while new fluorescence and phosphorescnce bands appeared at 512, 481, and 472 nm (λ_{ex}=358 nm) and 418 nm (λ_{ex}=300 nm). The fluorescence excitation spectrum of the photolyzed solution followed at 481 nm corresponds to the absorption spectrum of A^+MeO^- shown in Fig. 9. The phosphorescence spectrum was completely in agreement with that of the authentic sample of AH_2. After a 13-min irradiation at 77 K, the sample was thawed at room temperature and analyzed by means of HPLC. The formation of AH_2 (ca. 10% yield) was detected. No $(AH)_2$ was measured by means of HPLC.

In place of ethanol, methanol, 1-propanol, and 1-butanol were also useful for the solvents in which MeOA was photoionized to yield A^+MeO^- at 77 K. Meanwhile, the formation of A^+MeO^- was not detectable in the photolyses in 1-octanol, *t*-butyl alcohol, methylcyclohexane, and acetonitrile at 77 K. In smaller alcohols without bulky group(s), the methoxide anion generated photochemically as a counter anion of A^+ may interact with the surrounding alcohol molecules through hydrogen bonding, resulting in the stabilization of the methoxide anion. Since alcohols with long or bulky alkyl chains as well as aprotic solvents could not interact with the methoxide anion at 77 K, a rapid recombination reaction of A^+ and MeO^- may occur to yield original MeOA. In all the media used herein, small amounts of AH_2 (<10%) were formed in the photolyses of MeOA at 77 K.

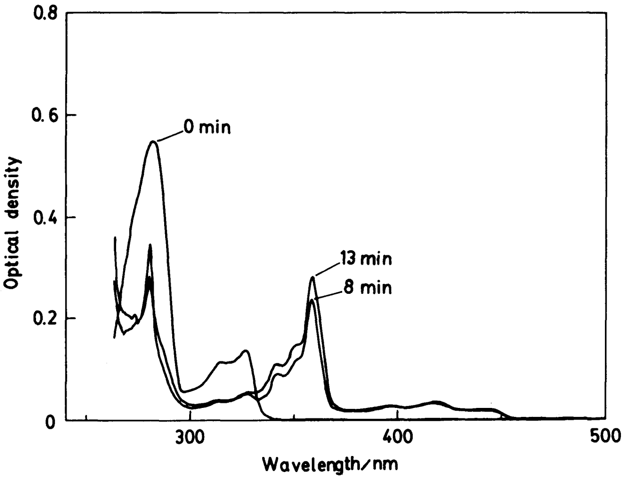


Fig. 9. Progressive absorption spectral changes of MeOA (5×10^{-5} M) in glassy ethanol upon irradiation with a 500 W super-high pressure Hg lamp at 77 K.

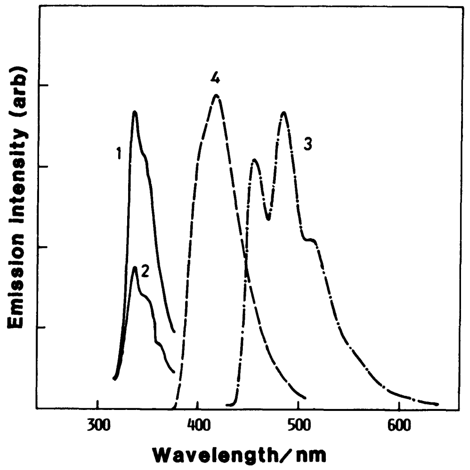


Fig. 10. Emission spectra of MeOA (5×10^{-5} M) and the photolyzed sample of MeOA in glassy ethanol at 77 K: 1 : MeOA before irradiation (λ_{ex}=288 nm), 2: MeOA after irradiation for 13 min (λ_{ex}=288 nm), 3: fluorescence of A^+MeO^- generated by the photolysis of MeOA (λ_{ex}=358 nm), 4: phosphorescence of AH_2 generated by the photolysis of MeOA (λ_{ex}=300 nm).

We can use the information obtained for the photolyses in rigid matrices to elucidate the reaction mechanisms of MeOA in fluid solutions. The heterolysis of MeOA may occur via the photoexcited singlet state of MeOA to give A^+MeO^-. Two competing reactions, the hydride transfer from MeO^- to A^+ forming AH_2 and formaldehyde (a most plausible product from MeO^-), and the recombination of A^+ and MeO^- regenerating MeOA, seem to proceed in fluid solutions:

$$\mathrm{MeOA} + h\nu \longrightarrow {}^1\mathrm{MeOA}^* \quad (5)$$

$$^1\mathrm{MeOA}^* \longrightarrow \mathrm{A}^+ + \mathrm{MeO}^- \quad (6)$$

$$\mathrm{A}^+ + \mathrm{MeO}^- \longrightarrow \mathrm{AH}_2 + \mathrm{HCHO} \quad (7)$$

$$\mathrm{A}^+ + \mathrm{MeO}^- \longrightarrow \mathrm{MeOA} \quad (8)$$

This mechanism for forming AH_2 can account for the formation of AH_2 in the photolysis of MeOA in acetonitrile (see Table 1). Of course, a two-step mechanism involving electron transfer, followed by hydrogen transfer, may account for the formation of AH_2 from A^+MeO^-:

$$\mathrm{A}^+ + \mathrm{MeO}^- \longrightarrow \mathrm{AH}\cdot + \mathrm{MeO}\cdot \quad (9)$$

$$\mathrm{AH}\cdot + \mathrm{MeO}\cdot \longrightarrow \mathrm{AH}_2 + \mathrm{HCHO} \quad (10)$$

This mechanism, however, seems inadequate for the reasons to be presentd below.

In the absence of oxygen, the photochemical reaction via the triplet state of MeOA becomes predominant. The major photoproduct of this case is $(AH)_2$. The most plausible precursor of $(AH)_2$ is the 9,10-dihydro-10-methylacridinyl radical (AH·). If the coupling reaction of these radicals provides $(AH)_2$ in the photolysis of MeOA, AH· should have a low ability to abstract a hydrogen atom from MeO· and/or the surrounding solvent molecule. The yield of $(AH)_2$ in 2-propanol is similar to those in methanol and acetonitrile, and no significant difference in the yield of AH_2 was observed between the hydrogen-donative alcohols and acetonitrile (see Table 1). The low ability of the acridinyl radical to abstract a hydrogen atom has also been found in the photolysis of acridine.[11,16] In the case of the photoreduction of acridine in hydrogen donative alcohols, a disproportionation of the 9,10-dihydroacridinyl radicals has been assumed for the mechanism of the 9,10-dihydroacridine formation (Eq. 2).[16] A possible mechanism for the $(AH)_2$ formation can be represented as:

$$^3\mathrm{MeOA}^* \longrightarrow \mathrm{AH}\cdot + \mathrm{MeO}\cdot \quad (11)$$

$$2\mathrm{AH}\cdot \longrightarrow (\mathrm{AH})_2 \quad (12)$$

$$2\mathrm{MeO}\cdot \longrightarrow \mathrm{MeOH} + \mathrm{HCHO} \quad (13)$$

The two-step mechanism, however, may still remain if a contact radical pair of AH· and MeO· is produced by the electron transfer from MeO^- to A^+ (Eq. 9) and if a subsequent hydrogen abstraction by AH· from MeO· (Eq. 10) occurs instantaneously. At the present stage, we cannot distinguish this two-step mechanism (a total hydride transfer mechanism) from the hydride transfer mechanism.

Conclusion

We have pesented mechanisms for the photochemical reactions of MeOA yielding AH_2 and $(AH)_2$. There is no doubt that the photolysis of a dilute methanolic solution of A^+Cl^- occurs via MeOA. The reaction mechanisms can be represented as Eqs. 5—8 and 11—13. At higher concentration of A^+Cl^-, the direct photoreaction of A^+Cl^- with methanol cannot be excluded because A^+Cl^- and MeOA coexist in the system. We found, however, that A^+Cl^- (5×10^{-5} M) in methanol containing 2×10^{-4} M HCl does not show any photochemical reaction. This indicates the absence of any reactivity of the 10-methylacridinium cation toward photolysis in the hydrogen-donative alcohol. The mechanism involving MeOA as an intermediate seems to be reasonable, even for the photolysis of A^+Cl^- at higher concentrations.

References

1) V. Zanker and P. Schmid, *Z. Phys. Chem. (Frankfurt am Main)*, **17**, 11 (1958).

2) V. Zanker and H. Schnith, *Chem. Ber.*, **92**, 2210 (1959).

3) F. Mader and V. Zanker, *Chem. Ber.*, **97**, 2418 (1964).

4) V. Zanker and G. Prell, *Ber. Bunsenges. Phys. Chem.*, **73**, 791 (1969).

5) P. Cerutti and M. Goth, *Angew. Chem.*, **76**, 54 (1964).

6) H. Göth, P. Cerutti, and H. Schmid, *Helv. Chim. Acta*, **48**, 1395 (1965).

7) A. Kellman, *J. Chim. Phys.*, **54**, 468 (1957).

8) A. Kellman, *J. Chim. Phys.*, **57**, 1 (1960).

9) S. Kato, S. Minagawa, and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **34**, 1026 (1961).

10) S. Niizuma and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **36**, 1629 (1963).

11) M. Koizumi, S. Niizuma, and T. Miyashita, *Z. Phys. Chem. (Frankfurt am Main)*, **71**, 165 (1970).

12) M. Hoshino, S. Niizuma, and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **45**, 2988 (1972).

13) A. Kira and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **42**, 625 (1969).

14) A. Kira, Y. Ikeda, and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **39**, 1673 (1966).

15) D. G. Whitten and Y. J. Lee, *J. Am. Chem. Soc.*, **93**, 961 (1971).

16) For example; M. Koizumi, S. Kato, N. Mataga, T. Matsuura, and Y. Usui, "Photosensitized Reactions," Kagaku Dojin, Kyoto (1978), Chap. 4.

17) V. Zanker, E. Erhardt, F. Mader, and J. Z. Thies, *Naturforsch. B*, **21**, 102 (1966).

18) K. Kano, B. Zhou, and S. Hashimoto, *Chem. Lett.*, **1985**, 791.

19) F. Kröhnke and H. L. Honig, *Chem. Ber.*, **90**, 2215 (1957).

20) J. Clark and M. Bakavoli, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 1966.

21) Y. Matsuoka and K. Yamaoka, *Bull. Chem. Soc. Jpn.*, **52**, 3163 (1979).

22) Y. Matsuoka and K. Yamaoka, *Bull. Chem. Soc. Jpn.*, **53**, 2146 (1980).

23) A. Hantzsch and M. Kolb, *Chem. Ber.*, **32**, 3109 (1899).

24) J. J. Dobbie and C. K. Tinkler, *J. Chem. Soc.*, **1905**, 269.

25) J. A. Aston, *J. Am. Chem. Soc.*, **53**, 1448 (1931).

26) J. W. Bunting and G. M. Kauffman, *Can. J. Chem.*, **62**, 729 (1984).

27) S. Shinkai, T. Tsuno, and O. Manabe, *J. Chem. Soc., Perkin Trans. 2*, **1984**, 661.

28) J. W. Bunting and W. G. Meathrel, *Can. J. Chem.*, **52**, 981 (1974).

29) N. Suzuki, Y. Kazui, T. Tsukamoto, M. Kato, and Y. Izawa, *Bull. Chem. Soc. Jpn.*, **56**, 1519 (1983).

30) N. J. Turro, "Modern Molecular Photochemistry," Benjamin/Cummings, Menlo Park, Calif. (1978), Chap. 8.