  Bull. Chem. Soc. Jpn., 61, 1633—1640 (1988)

Thermal and Photochemical Reactions of 10-Methyl-9-phenylacridinium Chloride in Alcohols

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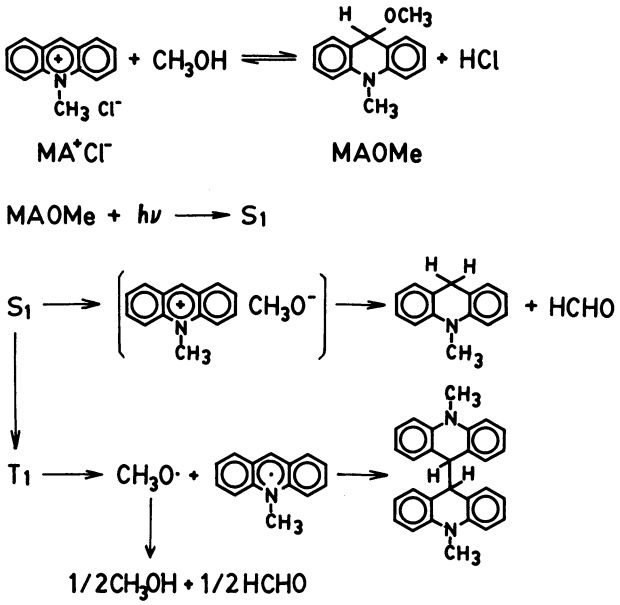
(Received July 13, 1987)

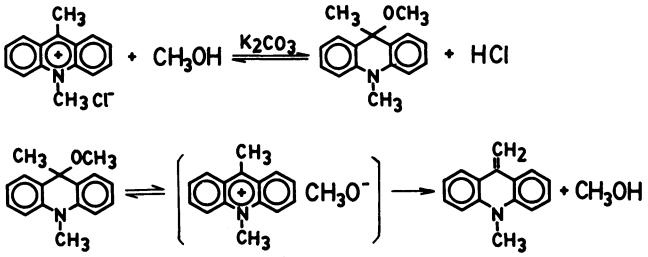
The photoreduction of 10-methyl-9-phenylacridinium chloride in methanol containing K_2CO_3 involves the nucleophilic addition of methanol to the 9-position of the acridinium cation, the photoinduced heterolysis of the methanol adduct, and the hydride transfer from the alkoxide anion to the acridinium cation in the nonrelaxed ground states to give 9,10-dihydro-10-methyl-9-phenylacridine.

In the previous paper, we postulated the photoreduction mechanism of 10-methylacridinium chloride (MA^+Cl^-) in methanol (Scheme 1):[1]



Scheme 1.

This mechanism is different from that for acridine whose n, π^* excited state can abstract a hydrogen atom from alcohols.[2] The mechanism involving the hydrogen abstraction of photoexcited acridinium cation from alcohols[3] is not understandable because the acridinium cation has no odd electrons which can participate in the n–π^* transition. Our mechanism can explain reasonably the formation of 9,10-dihydro-10-metylacridine (MAH_2) and 10,10′-dimethyl-9,9′, 10,10′-tetrahydro-9,9′-biacridinyl ($(MAH)_2$). From a different point of view, the reduction of the acridinium cation by alcohols is interesting because of its analogy with the $NADP^+$ alcohol dehydrogenase reactions. The light energy, however, needs to promote the reduction of MA^+Cl^- to MAH_2. One of the key steps to realize the $NADP^+$-mimic reaction is heterolysis of the alcohol adduct, which is formed by a nucleophilic attack of the alcohol to the carbon atom at the 9-position of the acridinium cation. A possibility to achieve spontaneous heterolysis of the alcohol adduct is utilization of strain energy at the 9-position of the acridine ring. Next we examined the reaction of 9,10-dimethylacridinium chloride (MMA^+Cl^-) with methanol.[4] Indeed, the methanol adduct provided by a K_2CO_3-catalyzed reaction of MMA^+Cl^- with methanol dissociates into MMA^+ and CH_3O^- in the dark. Unfortunately, however, a proton abstraction from the CH_3 group at the 9-position of MMA^+ of CH_3O^- proceeds to give 9,10-dihydro-10-methyl-9-methyleneacridine (Scheme 2):[4]



Scheme 2.

These aspects led us to study the reactions of 10-methyl-9-phenylacridinium chloride (MPA^+Cl^-) with alcohols. Although the $NADP^+$-mimic reactions could not be realized, we obtained important results which strongly support the photoreduction mechanism shown in Scheme 1.

Experimental

9-Phenylacridine (PA) was prepared by a Bernthsen method.[5] MPA^+Cl^- (mp 187—189 °C) was obtained by passing an aqueous solution of 10-methyl-9-phenylacridinium iodide, (which was prepared by the reaction of PA with methyl iodide), through a Dowex 1X8 ion-exchange column and recrystallization from water. 9,10-Dihydro-10-methyl-9-phenylacridine (mp 109—110 °C) (MPAH) was prepared according to procedures described in the literature.[6] 9,10-Dihydro-9-methoxy-10-methyl-9-phenylacridine (MPAOMe) was obtained by the following procedures. MPA^+Cl^- (1.6 g) in methanol (20 ml) was poured into methanol (50 ml) containing 1 M (1 M=1 mol dm^{-3}) NaOH and the solution was stirred for 5 min at room temperature. The colorless precipitates were filtered, washed with water, and recrystallized from hexane, giving MPAOMe (1.2 g, 74 %): mp 149—150 °C; ^1H NMR (acetone-d_6) δ=2.94 (3H, s, OCH_3), 3.57 (3H, s, N-CH_3), and 6.88—7.33 (13H, m,

aromatic); UV (C_2H_5OH) 332 (ε 4900), 319 (5100), 300 (sh), and 285 nm (19600). Found: C, 83.71; H, 6.29; N, 4.63%. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65%. All solvents used were of spectroscopic grades.

The absorption spectra were taken on a Shimadzu UV-200S spectrophotometer. The 400 MHz ^1H NMR spectra were measured by a JEOL JNM-GX400 spectrometer. The ESR spectrum was kindly measured by Professor K. Maruyama and Dr. T. Katagiri of Kyoto University using a JEOL PE-3X spectrometer. The methods of photolysis and analysis of the products have been described in the previous paper.[1]

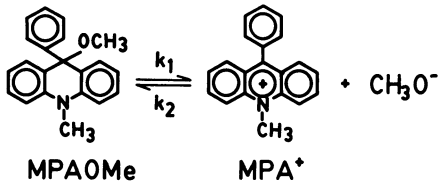
Results

Nucleophilic Addition of Alcohols to MPA$^+$Cl$^-$. Bunting and Meathrel[7] reported ^1H NMR of MPAOMe obtained from the reaction of MPA$^+$Cl$^-$ with sodium methoxide without mention of mp and yield. We also isolated and purified MPAOMe as is described in the Experimental Section.

A dilute methanolic solution of MA$^+$Cl$^-$ (1×10^{-5}M) does not show the characteristic absorption spectrum of the acridinium ion because most of MA$^+$Cl$^-$ molecules are converted to MAOMe.[1] As Fig. 1 shows, however, MPA$^+$Cl$^-$ in methanol exhibits the ^1L_a, ^1L_b, and ^1B_b transition bands due to the acridinium ring. Comparing the absorption spectrum of MPA$^+$Cl$^-$ in methanol with that in acetonitrile, it was found that an additional absorption band appears at around 285 nm in methanol. The spectrum of an authentic sample suggests that the absorption band with λ_{max} at 285 nm is ascribed to MPAOMe. Upon addition of K_2CO_3, MPAOMe was formed at the expense of MPA$^+$Cl$^-$ (Fig. 1).

The pseudo-first-order rate constants for the alcohol addition (k) and the infinite yield of the alcohol adducts could be determined from the changes in the optical densities of MPA$^+$Cl$^-$ (5×10^{-5} M) in alcohols containing K_2CO_3 (5×10^{-4}). The results are summarized in Table 1. The alcohol addition was depressed in the order of methanol, ethanol, 2-propanol, and t-butyl alcohol.

Spontaneous Heterolysis of MPAOMe. When MPAOMe (5×10^{-5} M) was dissolved in methanol, the intensity of the absorption band due to MPAOMe (285 nm) gradually decreased and the bands due to 10-methyl-9-phenylacridinium methoxide (MPA$^+$MeO$^-$) appeared at 362 and 424 nm. After a definite time, the system reached a stationary state where MPAOMe and MPA$^+$MeO$^-$ coexist:



(1)

The rate constant for the dissociation of MPAOMe (k_1) could be obtained from Eq. 2:

$$\ln\frac{C_e + C(1 - C_e/C_0)}{C_e - C} = \left(\frac{2C_0}{C_e} - 1\right)k_1 t \qquad (2)$$

where C_0 is the initial concentration of MPAOMe, C_e is the MPA$^+$MeO$^-$ concentration at the equilibrium state, and C is the MPA$^+$MeO$^-$ concentration at time t. Equation 2 can be applied to the reactions in methanol and aprotic solvents. When alcohols other than methanol are used, the exchange reactions such

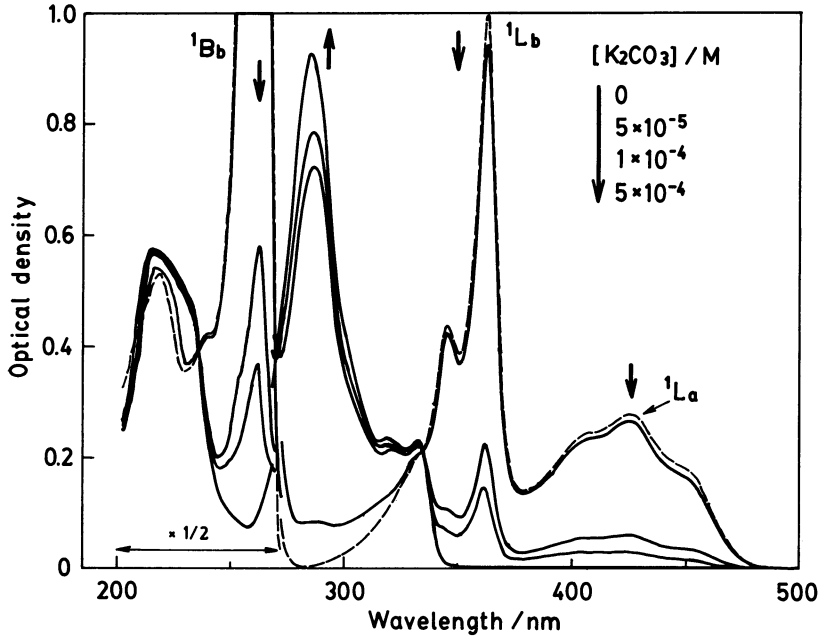


Fig. 1. Absorption spectra of MPA$^+$Cl$^-$ (5×10^{-5} M) in methanol with and without K_2CO_3 (——) and in acetonitrile (– – –) at 22 °C.

as $CH_3O^-+ROH \rightleftarrows CH_3OH+RO^-$ may take place necessitating a more complex treatment. The k_1 values in the methanol and acetonitrile are shown in Table 2 together with the yields of MPA^+MeO^- at the equilibrium states and the dissociation constants of MPAOMe (K_D). As Table 2 clearly indicates, the dissociation of MPAOMe occurs effectively only in methanol. This may be ascribed to the stabilization of the polar transition state and the ionic products by the polar protic solvent. A polar aprotic solvent, such as acetonitrile, is a poor solvent for dissociation because of the absence of a hydrogen bond between CH_3O^- and the solvent.

Although MPAOMe dissociates spontaneously to MPA^+MeO^- in methanol at room temperature, no formation of MPAH was detected by means of HPLC.

Photoinduced Heterolysis of MPAOMe. In the case of MAOMe, the photochemical dissociation of this pseudo base into MA^+MeO^- is observed only in a solvent matrix at 77 K[1,8] As is reported by Grigoreva et al.,[9] however, the photolysis of MPAOMe in aerated alcohols and acetonitrile at 22 °C caused the rapid formation of MPA^+MeO^-. The relationship between the yield of MPA^+MeO^-, which was determined by means of absorption spectroscopy, and the irradiation time is shown in Fig. 2. Figure 2 indicates that the formation of MPA^+MeO^- is saturated and photostationary states are reached. The yields of MPA^+MeO^- at the stationary states were 44% in methanol, 45% in ethanol, 49% in 2-propanol, and 17% in acetonitrile.

A 30-s irradiation of the ethanolic MPAOMe (5×10^{-5} M) solution gave MPA^+MeO^- in 12% yield. The dissociation was followed by a slow recombination to the alcohol adduct in the dark. After the recombination was completed, the photolyzed solution was analyzed by means of HPLC which reveals the formation of a trace amount of MPAH. For the photolysis of MAOMe in solution, we postulated the mechanism for formation of MAH_2 shown in Scheme 1.[1] If this mechanism is applicable for the photolysis of MPAOMe, it can be considered that the hydride transfer from CH_3O^- to MPA^+ occurs in low quantum yield. Although the 2-min irradiation of MAOMe (5×10^{-5}M) in aerated methanol provides MAH_2 and MA=O in 35 and 5% yields respectively, the yield of MPAH in the photolysis of MPAOMe under the same conditions is only <1%.

Photochemical Reactions of MPA^+Cl^- and MPAOMe in the Presence of K_2CO_3. Figure 3 shows the rates of MPAH formation when MPA^+Cl^- (5×10^{-5} M) in aerated methanol was irradiated in the absence and the presence of K_2CO_3. A slow photoreduction occurred in the absence of K_2CO_3, whereas the formation of MPAH was markedly accelerated by K_2CO_3. These results clearly indicate that MPAH is produced via

Table 1. Pseudo-First-Order Rate Constants for Nucleophilic Addition of Alcohols to MPA^+Cl^- (k) and Yields of Alcohol Adducts at Infinite Time at 22 °C[a]

Alcohol	$10^4\,k/s^{-1}$	Yield/%
Methanol	very fast	100
Ethanol	58.3±0.7	100
2-Propanol	7.55±0.03	100
t-Butyl alcohol[b]	4.77±0.11	58

a) The rate constants and the yields of the alcohol adducts were determined for the samples of 5×10^{-5} M MPA^+Cl^- in alcohols containing 5×10^{-4} M K_2CO_3. b) The concentration of K_2CO_3 was 3×10^{-4} M.

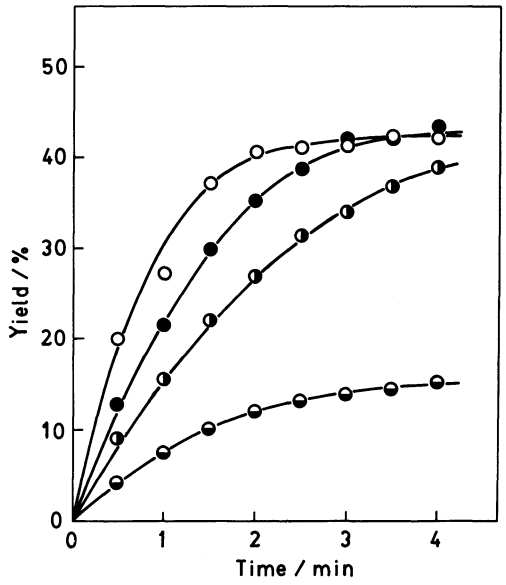


Fig. 2. Photoinduced dissociation of MPAOMe (5×10^{-5} M) to MPA^+MeO^- in methanol (○), ethanol (●), 2-propanol (◑), and acetonitrile (◒) without base at 22 °C. The ordinate is the yield of MPA^+MeO^-.

Table 2. First-Order Rate Constants for Dissociation of MPAOMe to MPA^+MeO^- (k_1), Yields of MPA^+MeO^- at Equilibrium States, and Dissociation Constants of MPAOMe (K_D) in Alcohols and Acetonitrile at 22 °C[a]

Solvent	$10^7\,k_1/s^{-1}$	Yield of MPA^+MeO^-/%	K_D/M
Methanol	7870±73	37	5000
Ethanol	(840±14)[b]	6	230
2-Propanol	(35.6±0.6)[b]	4	120
Acetonitrile	3.7±1.3	2	9

a) The initial concentration of MPAOMe was 5×10^{-5} M. b) The apparent k_1 value was obtained by assuming that the exchange reaction, $CH_3O^-+ROH=CH_3OH+RO^-$, does not occur (see text).

photolysis of MPAOMe. Under similar conditions, the photolysis of MPAOMe yielded MPAH (Fig. 4). Upon irradiation in methanol without K_2CO_3, about 50% of MPAOMe rapidly dissociated into MPA^+MeO^- which is inactive toward photoreduction. In the presence of K_2CO_3, however, the MPA^+ generated reverts instantaneously to the original MPAOMe which is the precursor of MPAH. The prolonged irradiation, therefor, seems to result in an accumulation of MPAH. The yield of MPAH was 68% when MPAOMe (5×10^{-5} M) in aerated methanol containing K_2CO_3 (5×10^{-4} M) was irradiated for 3 h. The photochemical behavior of MPAOMe in aerated ethanol was essentially the same as that in methanol (Table 3). In this case, MPA^+ photochemically generated may be attacked by surrounding ethanol to yield 9,10-dihydro-9-ethoxy-10-methyl-9-phenylacridine (MPAOEt) by the aid of K_2CO_3. MPAOEt may also be a precursor of MPAH.

As Table 3 shows, the yield of MPAH was significantly lowered during photolysis in aerated 2-propanol containing K_2CO_3. Since the nucleophilic attack of 2-propanol to MPA^+ is slower than the photoinduced heterolysis of MPAOMe (see Table 1), the formation of MPA^+MeO^- was detected by absorption spectroscopy at the initial stage of the photolysis. Prolonged irradiation caused the decomposition of MPA^+, giving small amounts of MA=O along with various unknown products. Complex photoreactions of MPAOMe also proceeded in aerated acetonitrile without K_2CO_3. From the photolyzed solution, PA and MA=O were isolated by means of a silica-gel column chromatography. These products were identified by ^1H NMR, absorption, and emission spectroscopy. The changes in the yields of MPAH, MA=O, and PA with irradiation time are shown in Fig. 5.

The yields of MPAH in the photolyses of MPAOMe decreased under anaerobic conditions (Table 3). The

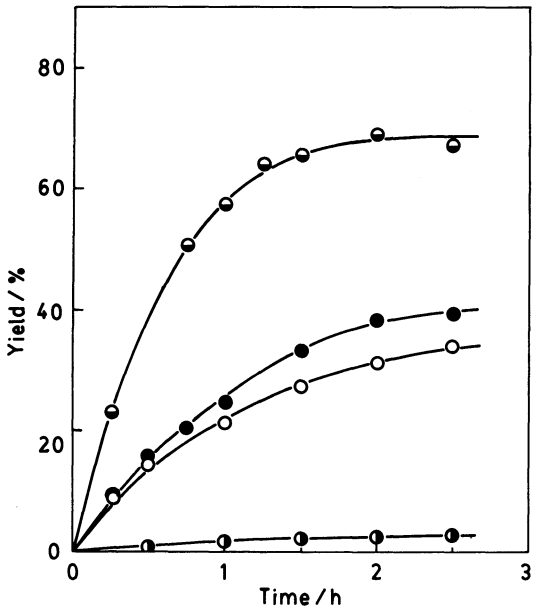


Fig. 3. Yields of MPAH in the photolyses of MPA^+Cl^- (5×10^{-5}) in aerated methanol in the absence (◑) and the presence of 5×10^{-5} (○), 1×10^{-4} (●), and 5×10^{-4} M (◒) K_2CO_3 at 22 °C.

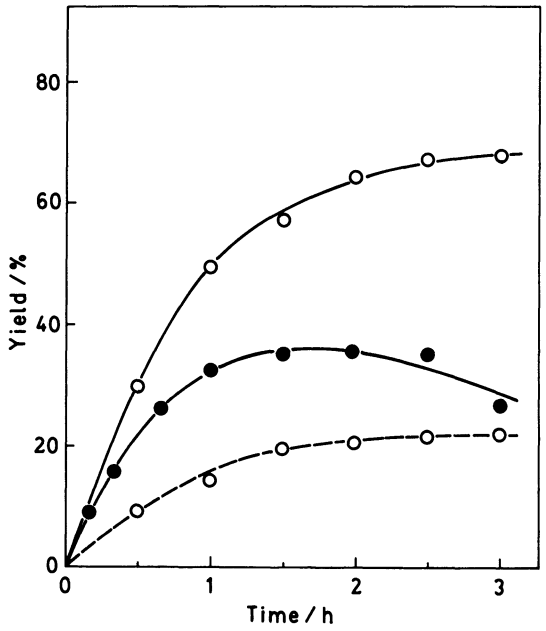


Fig. 4. Yields of MPAH in the photolyses of MPAOMe (5×10^{-5} M) in aerated (○) and deaerated methanol (●) in the absence (———) and the presence of 5×10^{-4} M K_2CO_3 (——) at 22 °C.

Table 3. Yields of MPAH, PA, and MA=O in Photolyses of MPAOMe in Solvents under Aerobic and Anaerobic Conditions and Lifetimes of MPA·(τ) Photochemically Generated at 22 °C[a]

Solvent	Irradiation time/min	Yield/%[b]			τ/min
		MPAH	PA	MA=O	
Methanol	90	66(35)	0(0)	0(0)	3.7
Ethanol	90	58(23)	0(0)	0(0)	27
2-Propanol	40	14(7)	0(0)	5(0)	55
Acetonitrile[c]	10	7(5)	15(8)	8(0)	16

a) The alcohols solutions of 5×10^{-5} M MPAOMe was irradiated in the presence of 5×10^{-4} M K_2CO_3. b) The values in parentheses represent the yields of the products obtained under anaerobic conditions. c) The MPAOMe (5×10^{-5} M) solution was irradiated in the absence of K_2CO_3.

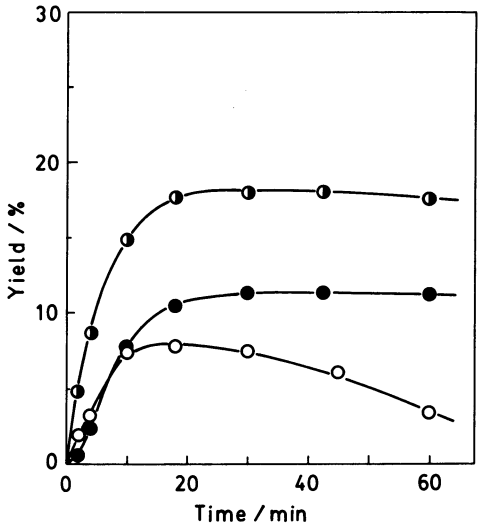


Fig. 5. Yields of MPAH (○), PA (◑), and MA=O (●) in the photolysis of MPAOMe (5×10^{-5} M) in aerated acetonitrile without base at 22°C.

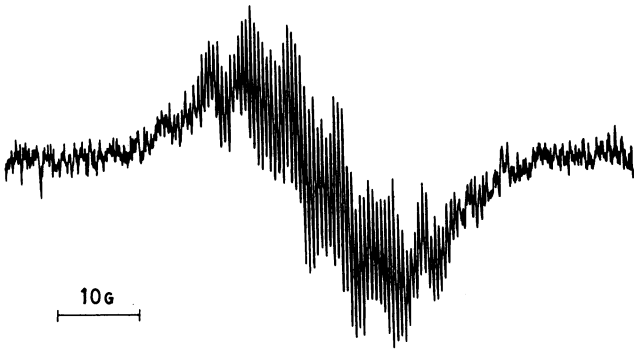


Fig. 6. ESR spectrum of MPA· generated by the photolysis of MPAOMe (5×10^{-4} M) in deaerated ethanol containing ca. 1×10^{-3} M K_2CO_3. The spectrum was measured after the solution was irradiated with a 500-W super high-pressure Hg lamp for ca. 20 s at room temperature.

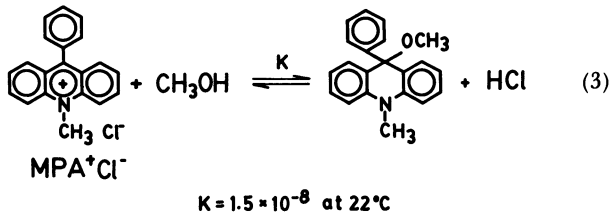
formation rate of MPAH in deaerated methanol containing K_2CO_3 is shown in Fig. 4. The initial rate in deaerated methanol was slightly slower than that in aerated methanol and the subsequent photodecomposition of MPAH proceeded. The HPLC analysis of the photolyzed solution indicated that various unknown products are produced along with MPAH upon irradiation in deaerated methanol. Most of these unknown products were the same as those produced by the photolysis of MPAH. During irradiation, the photolyzed solution became red-violet (λ_{max}=518 and 487 nm) which faded upon contact with air. The ESR spectrum (Fig. 6) clearly showed that the red-violet color is due to 10-methyl-9-phenylacridinyl radical (MPA·). The ESR spectrum shown in Fig. 6 is in good agreement with that of MPA· produced by electrochemical reduction of MPA+Cl⁻.[10] MPA· gradually disappeared in the dark. The lifetimes of MPA· in alcohols and acetonitrile are listed in Table 3.

Photochemical Reaction of MPAOMe in Ethanol Matrix at 77 K. MPAOMe (5×10^{-5} M) in an ethanol matrix at 77 K was irradiated for 70 min. The absorption spectrum indicated the disappearance of MPAOMe and the appearance of an absorption band having its maximum wavelength at 360 nm, which corresponds to that of PA. The HPLC analysis showed the formation of MPAH and PA in 29 and 15% yields, respectively.

Thermal Reaction of MPAOMe in Methanol and Acetonitrile. The acetonitrile solution of MPAOMe (5×10^{-5} M) was refluxed for 3.5 h under the aerobic conditions. The reaction mixture became yellowish during heating and the formation of MPA+MeO⁻ (ca. 80% yield) was confirmed by absorption spectroscopy. Interestingly, MPAH, MA=O, and PA were also produced in 11, 2, and 8% yields, respectively. Any other products were not detected by HPLC. Under anaerobic conditions, however, no MPA+MeO⁻ was formed and MPAH (2%) was the sole product which was detectable by HPLC, while most of the MPAOMe decomposed in refluxing acetonitrile. No generation of MPA· was observed by absorption spectroscopy. Although the dissociation of MPAOMe to MPA+MeO⁻ occurred in boiling methanol under aerobic conditions, neither MPAH nor MA=O and PA were produced. In the presence of K_2CO_3, MPAOMe in boiling methanol did not react at all.

Discussion

It is well-known that the electrophilicity of 10-alkylacridinium cations is so strong that nucleophiles such as hydroxide and alkoxide anions attack the carbon atom at the 9-position of the acridinium ring to give corresponding pseudo bases.[11–19] Bunting et al.[7,17] have found that the nucleophilic addition of OH^- to the 9-aryl-10-methylacridinium cations occurs about 30-fold faster than that to the corresponding triphenylmethyl cation analogues and the bulky substituents at the 9-position do not seriously prevent the addition of OH^-. In the present study, we isolated and purified the methanol adduct of MPA+Cl⁻, MPAOMe, in moderate yield (see Experimental Section). It was also found that an equilibrium shown in Eq. 3 is established in methanol even in the absence of base:

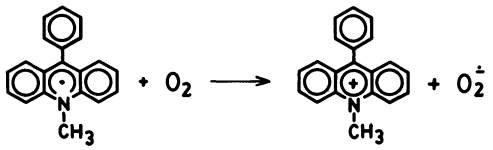


(3)

In dilute solution, MPA+Cl⁻ could be converted quantitatively to MPAOMe in methanol in the presence of K_2CO_3 (see Table 1). As Table 1 shows, the addition of alcohols to MPA+Cl⁻ is greatly affected by the kind of alcohol. Since the positive charge of the acridinium cation distributes in the transition state, the nucleophilic addition of alcohol is expected to be accelerated in a nonpolar solvent. The experimental results, however, are opposite to this expectation. One of the factors which dominates the alcohol addition may be a steric hindrance. The hydrogen atoms at the 1- and 8-positions as well as the phenyl substituent at the 9-position of the acridinium ring may inhibit ability to reach the transition state. Meanwhile, since the carbon atom at the 9-position of the alcohol adducts is a sp^3 orbital, the steric hindrance is greatly weakened. The alcohol adducts, therefore, are considerably more stable in the cases of the primary and secondary alcohols when a weak base is present in the system.

We expected the spontaneous heterolyses of the alcohol adducts followed by the hydride transfer from the alkoxide anions to MPA+. The spontaneous heterolyses could be realized in alcohols and acetonitrile (see Table 2). As is expected theoretically, the dissociation of MPAOMe into MPA+MeO⁻ favors a polar protic solvent such as methanol. In ethanol, 2-propanol, and acetonitrile, however, MPAOMe hardly dissociates. Since the phenyl ring at the 9-position of MPA+ is not coplanar with the acridinium ring, the change in the hybrid orbital of the carbon atom from sp^3 to sp^2 upon dissociation of MPAOMe to MPA+MeO⁻ seems to require relatively large energy. Although the spontaneous heterolysis of MPAOMe in methanol was appreciable, the hydride transfer between MPA+ and CH_3O^- does not occur at all.

MPAH could be obtained photochemically from MPAOMe. In aerated methanol without base, the photolysis of MPAOMe led to the effective heterolysis to MPA+MeO⁻ and the ineffective reduction to MPAH (see Fig. 2). In the presence of K_2CO_3, the photochemical formation of MPAH became a predominant reaction (see Fig. 4 and Table 3). Under anaerobic conditions, the formation of MPAH was depressed because of the photodecomposition of MPAH (see Fig. 4). If the photoreduction proceeds by a radical mechanism via the triplet state of MPAOMe, the rate of the MPAH formation should be faster, at least at the initial stage of the photolysis, in deaerated methanol than in aerated methanol. The experimental results disagree with this expectation (see Fig. 4). It can be concluded, therefore, that an ionic mechanism via the lowest excited singlet state of MPAOMe accounts for the formation of MPAH. In photolyses under anaerobic conditions, however, the formation of MPA· was detected by adsorption and ESR spectroscopy. In the presence of oxygen, MPA· is expected to be quenched (Eq. 4) or converted to MA=O (Eq. 5):



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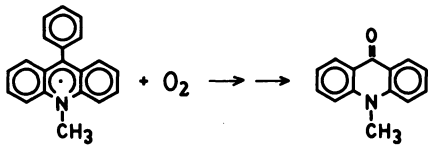
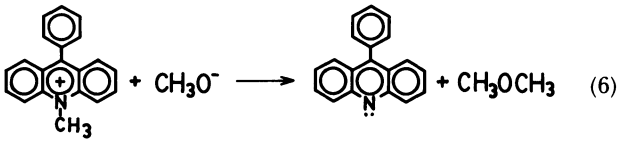


(5)

Indeed, small amounts of MA=O were produced in the photolyses of MPAOMe in aerated 2-propanol and acetonitrile (see Table 3). In neither methanol and ethanol, could MA=O be detected. Another reaction of MPAOMe in acetonitrile is the elimination of the CH_3 group at the 10-position of the acridine ring to give PA. The most plausible mechanism for the PA formation is S_N2 reaction between MPA+ and CH_3O^- photochemically generated:

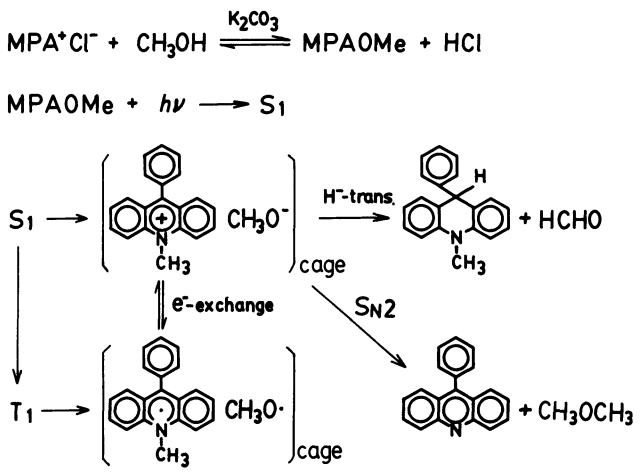


(6)

PA was not produced in alcoholic solutions (see Table 3). This may be due to the stabilization of CH_3O^- by strong solvation with alcohols through hydrogen bonding.

Important information was obtained from the photolysis of MPAOMe in an ethanol matrix at 77 K. In the rigid matrix, the formation of MPA+MeO⁻ and MPA· was not observed by the absorption spectroscopy. The main photoproducts are MPAH and PA. MPA+MeO⁻ photochemically generated should be a contact ion pair without solvation in the rigid matrix. Such an ion pair, therefore, is so active that the recombination to MPAOMe, the hydride transfer from CH_3O^- to MPA+ giving MPAH and formaldehyde, and the S_N2 reaction giving PA and CH_3OCH_3 are expected to occur competitively.

Let us return to the mechanism in fluid solutions. A plausible mechanism for the photoreaction of MPA+Cl⁻ in methanol is shown in Scheme 3. In the presence of base, photochemically inactive MPA+Cl⁻ is converted to MPAOMe which dissociates into MPA+MeO⁻ from its lowest excited singlet state. Most of the ion pairs in the Franck–Condon ground states will be solvated rapidly by a polar solvent. It seems that a part of the ion pairs in the nonrelaxed states transfers a hydride from CH_3O^- to MPA+ to give MPAH even in very low quantum yield. Solvated MPA+MeO⁻ is inactive and MPA+ is returned to the original MPAOMe by the aid of K_2CO_3. In both 2-



Scheme 3.

propanol and acetonitrile, the formation of the alcohol adduct is so slow that the electron transfer from CH_3O^- to MPA$^+$ takes place to generate MPA$\cdot$ and $CH_3O\cdot$ whose subsequent reactions may provide MA=O and unknown products. Since the electron transfer occurs through a long-distance interaction between MPA$^+$ and CH_3O^-, the formation of MPA$\cdot$ and $CH_3O\cdot$ may not be inhibited so sereously as hydride transfer from CH_3O^- to MPA$^+$ by solvation. MPA$\cdot$ therefore, was generated in all solvents tested in the present study under anaerobic conditions.

Another mechanism for MPAH formation is a radical mechanism which involves the homolysis of MPAOMe in the lowest excited singlet state to yield a singlet radical pair, MPA$\cdot$MeO$\cdot$, and subsequent hydrogen abstraction of MPA$\cdot$ from $CH_3O\cdot$ to form MPAH. This mechanism can be excluded on the basis of the results on the thermal reactions of MPAOMe in boiling methanol and acetonitrile. Although no reaction of MPAOMe occurred in aerated methanol except for the dissociation to MPA$^+$MeO$^-$, the products which are the same as those in the photolysis (MPA$^+$MeO$^-$, MPAH, MA=O, and PA) were obtained in refluxing acetonitrile. Under anaerobic conditions, heating in acetonitrile provided unknown products along with a small amount of MPAH; neither MPA$^+$MeO$^-$ nor MPA$\cdot$ was detected. If the thermal reaction of MPAOMe to MPAH proceeds via the singlet radical pair, MPAH should also be produced in the reaction of MPAOMe in boiling methanol because the yield of MPAH photochemically formed is higher in methanol than in acetonitrile. The solvent effect on the thermal reaction of MPAOMe can be interpreted in terms of the ionic mechanism, but not the radical mechanism. Since acetonitrile is an aprotic polar solvent, the stabilization of CH_3O^- by this solvent should be much weaker than by methanol. The thermal dissociation of MPAOMe to MPA$^+$MeO$^-$, therefore, may be followed by the hydride transfer and the nucleophilic substitution to give MPAH and PA, respectively, in boiling acetonitrile. Presumably, an electron transfer from CH_3O^- to MPA$^+$ occurs to generate the radical pair composed of MPA$\cdot$ and $CH_3O\cdot$. Under aerobic conditions, MPA$\cdot$ should be quenched by oxygen to regenerate MPA$^+$ (see Eq. 4). In the absence of oxygen, however, the radical species may induce complex reactions to give unknown products in refluxing acetonitrile. It can be concluded, therefore, that the radical pair, MPA$\cdot$CH$_3$O$\cdot$ is not a precursor of both MPAH and PA. It is clear that the solvation to MPA$^+$MeO$^-$ plays an important role to promote the subsequent hydride transfer and nucleophilic substitution reactions. In alcoholic solvents, CH_3O^- generated as a counter anion of MPA$^+$ is stabilized so extensively by alcohols through hydrogen bonding that neither intramolecular hydride transfer nor nucleophilic substitution of MPA$^+$MeO$^-$ take place. The photochemical processes of MPAOMe, however, can provide a nonrelaxed ground state of MPA$^+$MeO$^-$ to promote hydride transfer to form MPAH.

The present study was supported by Grant-in-Aids for Science Research No. 61550647 from the Ministry of Education, Science and Culture.

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