BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 255—257 (1969)

Reactive States of Acridine in Alcohols and the pK Value of T(n–π^*) State as judged from the pH Dependence of the Photoreduction Quantum Yield

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(Received April 23, 1968)

Previous work[1–5] on the photoreduction of acridine (A) in various alcohols has established that the reactive states are in general the singlet excited state S* and the triplet n–π^* state T_2 and that for each reactive state there are molecular (M) and radical (R) mechanisms; therefore generally speaking, four schemes, S*R, S*M, T_2R and T_2M participate in the reaction.

In this paper the similar problem is attacked from a different point of view for methanol, ethanol and isopropanol. As is well-known, pK_A of the ground state, S* and triplet π–π^*, T_1 are respectively 5.45,[6] 10.65[6] and 5.6[7] (for T_2, not known) and the acridinium ion (AH^+) is non-reactive;[8] hence, it is expected that the pH dependence of the photoreduction quantum yield, Φ reflects the pK_A's of the reactive state, provided the equilibrium state were realized in the excited state.

With such a view, the pH depencence of fluorescence and of Φ was investigated at first, using the water-alcohol mixture buffered with (CH_3COONa, HNO_3), (KH_2PO_4, Na_2HPO_4) and (Na_2CO_3, $NaHCO_3$). Taking into account the effect of alcohol on pH-values and Φ in the water-alcohol mixture, the volume ratio of water and alcohol was chosen as 2 : 1. The concentration of acridine was 1×10^{-4} M. Fluorescence was measured by an Aminco Bowman spectrofluorimeter. Since the fluorescence of AH^+ (peak at 470 nm) is very weak at the peak position of A (420 nm), the intensity at 420 nm was taken as the intensity of A. Reaction rate was investigated by illuminating the solution by 365 nm light and by measuring the intensity

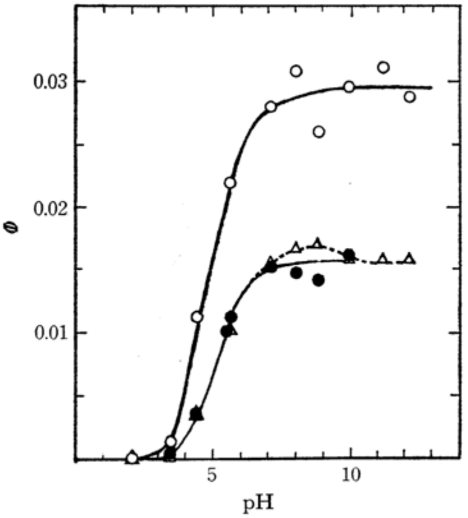

Fig. 1. pH dependence of Φ and I_F in water-ethanol (2:1 in vol).
[A] = 1×10^{-4} M Temperature: 25°C
—○— Φ, deaerated solution
—●— Φ, aerated solution
···△··· I_F, aerated solution

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2) A. Kellmann, *J. chim. phys.*, **63**, 936 (1966).

3) A. Kira, Y. Ikeda and M. Koizumi, This Bulletin, **39**, 1673 (1966).

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5) M. Koizumi, Y. Ikeda and T. Iwaoka, *J. Chem. Phys.* **48**, 1869 (1968).

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8) V. Zanker and H. C. Cnocloch, *Z. Naturforsch.*, **176**, 819 (1962).

of the transmitted 365 nm light.*[1] In all cases $\ln(e^D-1)$ - t plot (D, optical density) was satisfactorily linear at least in the initial stage, showing that the reaction is simple with the rate only proportional to the light absorption.

The results, as shown in Fig. 1, clearly show the sharp change around pH ~5 for both the fluorescence intensity (I_F) and Φ. These results indicate that with the usage of the ordinary buffer solutions, the equilibrium in the ground state is still maintained in the excited state. A small change of I_F around pH 9.5 may be due to the quenching action of some inorganic ions. Twice as large Φ in the degassed solution as that in the aerated solution is interpreted to be due to the participation of S*R mechanism and perhaps also of T_2R in the reaction.

Since the acid-base equilibrium specific to the excited state was not realized in the ordinary buffer solution, it has been undertaken next, following Weller,[6] to use NH_4^+ as a proton donor for accelerating the proton transfer and to investigate the effect of $[NH_4^+]$ upon the fluorescence and upon Φ. Fixing $[NH_3]/[NH_4^+]=0.1$ (buffer consisting of NH_3 and NH_4NO_3, pH=8.2, log $[AH^+]/[A]=-2.75$ in the ground state), the concentration of NH_4^+ was changed from 0.01 M to 2 M.

It was found that with the increase of $[NH_4^+]$, the fluorescence spectrum gradually changes from that of A to AH^+ with a clear isosbestic point, indicating the occurrence of Reaction $A^*+NH_4^+\rightarrow AH^{+*}+NH_3$. The quenching constants of NH_4^+ for the fluorescence of A, in methanol, ethanol and isopropanol were respectively 2.7, 1.7 and 1.2.*[2] Oxygen showed no quenching action. Φ was found also to decrease significantly by the increase of $[NH]_4^+$, as shown in Fig. 2. In this figure, I_F's (I_F at $[NH_4^+]=0.01$ M being normalized to the Φ-value at the same NH_4^+ concentration) are also plotted.

The very good agreement of the I_F- and Φ-plots for the aerated solutions for all alcohols, indicates that the reactive state in the aerated solution, is only S* (see below also). This is in complete agreement with the conclusion given in the previous paper.[4] In the aerated solution, radical mechanisms being eliminated, only S*M and T_2M mechanisms are possible, but the present results rule out the latter.

For the degassed solution, the S*R process contributes to the reaction, but this does not cause any difference between the I_F- and Φ-plots; hence it is only necessary to discuss the participation of T_2. When T_2 participates in the reaction in addition to S*, Φ at $[NH_4^+]=0.01$ M and at an arbitrary value of $[NH_4^+]$ may be put as follows,

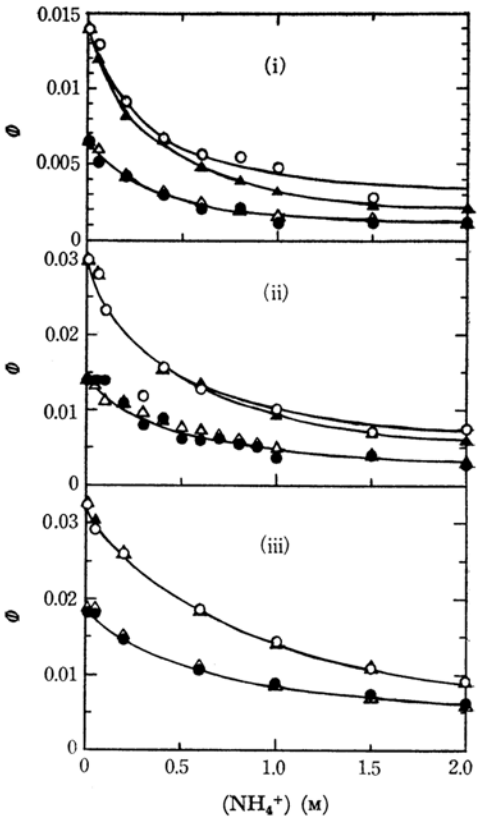

Fig. 2. Dependence of Φ and I_F on the concentration of buffer (NH_4NO_3-NH_3).
$[A]=1\times10^{-4}$ M Temperature: 25°C
(i) water-methanol (2:1 in vol.)
(ii) water-ethanol (2:1 in vol.)
(iii) water-isopropanol (2:1 in vol.)
—○— Φ, deaerated solution
—●— Φ, aerated solution
—▲— I_F, deaerated solution
—△— I_F, aerated solution

$$\Phi_0=(k_r+k_{ST}f^0)/k_e+k_d+k_r \qquad \text{for } 0.01\,\text{M of } [NH_4^+] \tag{1}$$

$$\Phi=(k_r+k_{ST}f+k_Q[NH_4^+]\varphi'_{ST}f')/k_e+k_d+k_r+k_Q[NH_4^+] \tag{2}$$

where k_e, k_d, k_r and k_{ST} are respectively the rate constant for emission, deactivation (including intersystem crossing), photoreaction and for intersystem crossing and where k_Q is the rate constant for Process $A^*+NH_4^+\rightarrow AH^{+*}+NH_3$*[3] and φ'_{ST} is

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*[1] The reaction product was judged from UV spectra to be acridan or the like in the aerated solution while in the degassed solution, diacridan was also produced, as judged from the appearance of white precipitate.

*[2] These values may be correlated with the viscosity of the solvents (Viscosities of the three alcohols at 30°C are 0.51, 1.00 and 1.76 in the above sequence).

*[3] The contribution of the backward reaction, $AH^++NH_3\rightarrow A+NH_4^+$ may be neglected, since the I_{F0}/I_F-$[NH_4^+]$ plot does not deviate much from the Stern-Volmer plot even at high NH_4^+ concentrations.

the intersystem crossing probability for AH^+. f_0 is a probability (an eventual fraction) for one A_{T_2} molecule produced from S*, to undergo reaction at $[NH_4^+]=0.01$ M. $f\,(f')$ is the similar probability for A_{T_2} ($AH^+{}_T$) (as to the assignment of $AH^+{}_T$, see below) at $[NH_4^+]>0.01$ M and $f=f_0$ ($f'=0$) or $f<f_0$ ($f'>0$), depending upon whether A_{T_2} ($AH^+{}_T$) produced from S* has no probability or some probability of going to $AH^+{}_T$ (A_{T_2}). The situations can be described quantitatively as follows. The ratio of the quantities of A_{T_2} and $AH^+{}_T$ produced from S* (per unit time), may be approximated as $k_{ST}/k_Q[NH_4^+]\varphi'_{ST}$ and according to the relation,

$$k_{ST}/k_Q[NH_4^+]\varphi'_{ST} \lesseqgtr ([A_{T_2}]/[AH_T^+])_{eq} = K_{T_2}/[H^+] \quad (3)$$

the values of f and f' will be specified as follows,

$$\begin{cases} f=f_0 \\ f'>0 \end{cases} (\text{for} <) \quad \begin{cases} f=f_0 \\ f'=0 \end{cases} (\text{for} =) \quad \begin{cases} f<f_0 \\ f'=0 \end{cases} (\text{for} >) \quad (4)$$

From (1) and (2) the following relation can be derived straightforwardly.

$$(\Phi/\Phi)/(I_F/I_{F_0}) = \frac{k_r + k_{ST}f + k_Q[NH_4^+]\varphi'_{ST}f'}{k_r + k_{ST}f_0} \quad (5)$$

Three cases are discriminated from (5),

case a): $(\Phi/\Phi_0) > (I_F/I_{F_0})$

case b): $(\Phi/\Phi_0) = (I_F/I_{F_0})$

case c): $(\Phi/\Phi_0) < (I_F/I_{F_0})$

depending upon the following criterion,

$$k_{ST}f + k_Q[NH_4^+]\varphi'_{ST}f' \gtreqless k_{ST}f_0 \quad (6)$$

which in turn, depends upon (4) and accordingly upon (3).

The correlation between (3) and (4) is, however, purely mathematical, and from the practical viewpoint, one may safely say as follows from (6) in conjunction with (3) and (4).

i) Case a) occurs when pK_{T_2} is much smaller than ~8 and φ'_{TS} is not so small. ii) Case b) occurs when pK_{T_2} is similarly small and $\varphi'_{ST}\approx 0$, or when S* is an only reactive state.[*4]

Turning back to the experimental results, case a) fits for methanol and ethanol, and case b) for isopropanol. From the above criterion, it is concluded that for isopropanol S* is an only reactive state and for methanol and ethanol, T_2 also participates in the reaction. The larger difference between (Φ/Φ_0) and (I_F/I_{F_0}) for methanol than for ethanol, as seen in Fig. 2, implies the larger contribution of T_2 in the former case. All these conclusions are in complete agreement with the ones in the previous paper.[4)]

Furthermore, the present investigation strongly suggests that pK_{T_2} is much less than ~8. This view is further supported from the holding of case a) or case b) throughout the whole range of $[NH_4^+]$, because if pK_{T_2} is near ~8, (6) requires the change from case c) to case b) and further to case a) with the increase in $[NH_4^+]$.

The values of $k_Q\varphi'_{ST}f'/(k_r+k_{ST}f_0)$, as estimated from the plot $(\Phi/\Phi_0)/(I_F/I_{F_0})$ *vs.* $[NH_4^+]$ is 0.2—0.3 for methanol. Although these values are not very reliable, yet, there is no doubt that both φ'_{ST} and f' are quite large. This is very important for characterizing $AH_T{}^+$. Firstly, a large value of f' implies the rapid occurrence of Reaction $AH^{+*}\rightarrow A_{T_2}+H^+$, and this is only possible *via* some higher $T(\pi\text{–}\pi^*)$ state or $T(\sigma\text{–}\pi^*)$ state of AH^+. The former, however, is very unlikely, because Process $AH^+{}_T(\pi\text{–}\pi^*)\rightarrow A_T(n\text{–}\pi^*)+H^+$ is the one between different electronic states and may not favorably compete with the transition to the lowest $AH^+{}_T\,(\pi\text{–}\pi^*)$. Then the quite large value of φ'_{ST} implies that the $T(\sigma\text{–}\pi^*)$ state which in general is highly located, is in the present case, at least lower than AH^{+*}. It is worth while to add that the present technique, at least in principle, enables us to determine the pK value pertaining to $AH^+{}_T(\sigma\text{–}\pi^*)\rightleftarrows A_T(n\text{–}\pi^*)+H^+$.

The authors are gratefull to Professor H. Kokubun for fruitful discussion.

[*4] Case c) holds when pK_{T_2} is much larger than 8 and φ'_{ST} is not so large.