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KINETIC ISOTOPE EFFECT IN THE CHEMILUMINESCENT OXIDATION OF ACRIDAN BY DIBENZOYLPEROXIDE

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In the reaction between acridan (AH_2) and dibenzoylperoxide (DBP) yielding acridine (A) and benzoic acid 2 electrons and 2 protons are transferred from AH_2 to DBP. The lack of influence of radical inhibitors on the rate of product formation and the dependence of the reaction rate on the polarity of the medium were taken as evidence for a simultaneous transfer of the 2 electrons (1). Protonated acridine was identified as the electronically excited reaction product on the basis of the identity of the chemiluminescence emission spectrum and the fluorescence spectrum of the acridinium cation (1). However, additional experiments concerning the pH-profile of the spectrum and the intensity of the chemiluminescence suggested a selective excitation of protonated acridine supposed to be related to a specific configuration of the transition complex of the reaction.

RESULTS AND DISCUSSION

The chemiluminescence quantum yield was determined as a function of hydrogen ion concentration in the pH-range of o.6o to 8.85 (FIG. 1). Within this pH-range the shape of the chemiluminescence emission spectrum was found to be constant and identical to the fluorescence spectrum of protonated acridine. Since neutral and protonated acridine differ with respect to their emission spectra (2) a 2-step mechanism for the production of the excited reaction product according to

$$AH_2 + DBP \xrightarrow{\text{slow}} A^{*} + 2\ \text{Ø}CO_2H$$

$$A^{*} + \text{Ø}CO_2H \xrightarrow{\text{fast}} AH^{+*} + \text{Ø}CO_2^{-}$$

can be excluded.

In addition, the non-identity of the chemiluminescence pH-dependence with the pH-dependence of the acridinium cation fluorescence indicates a distinct difference in the acid-base characteristics of the excited reaction product and the excited acridinium cation. Since DBP is decomposed in basic solution and since the rate of decomposition increases with increasing pH an exact determination of the pK of the electronically excited reaction product is difficult.

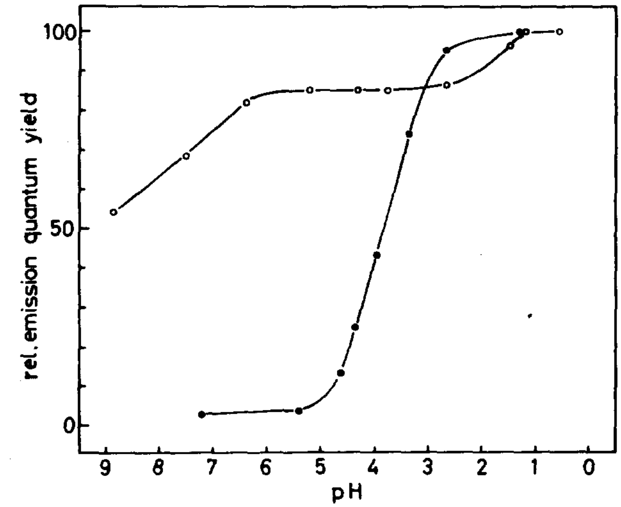


FIG. 1. pH-dependence of the acridinium cation fluorescence (●) and chemiluminescence (o) quantum yield in PrOH-H_2O 1:2 at 5o° C. Above pH 4 the solutions contain phosphate as buffer.

However, its pK_a must be at least 5 orders of magnitude larger than the pK_a of the excited acridinium ion as produced by the absorption of a light quantum. This fact indicates a transition type complex instead of the free acridinium cation as the emitter in the AH_2-DBP reaction. Within this complex acridine exhibits a basicity enhanced by a factor of about $1o^5$ as compared to free acridine.

There is an additional pK at 1.8 the nature of which is poorely understood. Possibly it involves the protonation equilibrium

$$[AH^+\text{-}\emptyset CO_2^-\text{-}\emptyset CO_2H]^* + H^+ \rightleftharpoons [AH^+\text{-}\emptyset CO_2H\text{-}\emptyset CO_2H]^*$$

On the basis of Stern-Volmer plots of the chemiluminescence quenching by DMSO at pH 4 and pH 1 the life times of these 2 hypothetical species are identical. However, the life time of the complex(es) differs from the life time of the excited free acridinium cation by a factor of 1.2 (TAB. 1). This small difference suggests that the low value of the total chemiluminescence quantum yield of the order of $1o^{-7}$ Einstein/mole is not caused by a low value of the emission yield (fluorescence yield of protonated acridine in PrOH-H_2O 1:2 at 5o° C o.49) but must be due to the excitation process being inefficient.

TAB. 1. Stern-Volmer quenching constants. Solvent PrOH-H_2O 1:2 at 45° C.

Quencher	Chemiluminescence, K ($lmole^{-1}$)	Fluorescence, K ($lmole^{-1}$)
DMSO	26	33
NH_4Cl	1o5	121

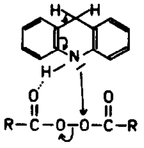
TAB. 2. Rate constants and quantum yields for the reaction of AH_2 and AD_2 with DBP at 50° C. |Dioxane| = 0.8 vol%.

System	Solvent	Rate constant ($l mole^{-1} min^{-1}$)	Total quantum yield (Einstein/mole)	Rel. emission yield	Rel. excitation yield
AH_2 + DBP	$PrOH-H_2O$ 1:2 |AcOH|=0.17M	$6.7_4 x 10^3$	$3.3 x 10^{-7}$	1.00	1.00
AD_2 + DBP	$PrOH-H_2O$ 1:2 |AcOH|=0.17M	$6.7_0 x 10^3$	$1.2 x 10^{-7}$	1.08	0.3_3
AH_2 + DBP	$PrOD-D_2O$ 1:2 |AcOD|=0.17M	$6.7_6 x 10^3$	$4.6 x 10^{-7}$	1.31	1.0_6
AD_2 + DBP	$PrOD-D_2O$ 1:2 |AcOD|=0.17M	$6.7_5 x 10^3$	$1.6 x 10^{-7}$	1.44	0.3_3

TABLE 2 summarizes the second order rate constants and the quantum yields of the reaction of AH_2 and 9.9'-dideuteroacridan (AD_2) with DBP in 1-propanol-water ($PrOH-H_2O$) 1:2 (v/v) and monodeutero-1-propanol(OD)-deuteriumoxide ($PrOD-D_2O$) 1:2 (v/v) at 50° C.

Within experimental error the rate constants for the 4 systems are identical whereas an isotope effect on excitation quantum yield is observed for the case of C-9 deuteration. These findings indicate that the breaking of the C-H bond at the 9-position of AH_2 is not rate determining. Furthermore, if differences in polarity, hydrogen bonding capacity, and viscosity between $PrOH-H_2O$ and $PrOD-D_2O$ are disregarded the possibility of the breaking of the N-H bond being rate determining is excluded as well.

As the initial step in the formation of the transition complex, the mechanism presented involves a transfer of the non-bonded electron pair from the nitrogen of AH_2 to one of the peroxidic oxygen atoms of DBP:



The formation of the transition complex is assumed to be rate determining. Second order kinetics result, first order with respect to AH_2 and DBP, respectively, if k_2 to k_4 are large as compared to k_1:

$$AH_2 + DBP \quad \underset{k_2}{\overset{k_1}{\rightleftarrows}} \quad [AH_2\text{-}DBP]$$

$$[AH_2\text{-}DBP] \quad \xrightarrow{k_3} \quad [AH^+\text{-}\emptyset CO_2^-\text{-}\emptyset CO_2H]$$

$$[AH_2\text{-}DBP] \quad \xrightarrow{k_4} \quad [AH^+\text{-}\emptyset CO_2^-\text{-}\emptyset CO_2H]^*$$

$$[AH^{+}\text{-}ØCO_2^{-}\text{-}ØCO_2H] \xrightarrow{k_5} AH^{+} + ØCO_2^{-} + ØCO_2H$$

$$[AH^{+}\text{-}ØCO_2^{-}\text{-}ØCO_2H]^{*} \xrightarrow{k_6} AH^{+} + ØCO_2^{-} + ØCO_2H$$

$$[AH^{+}\text{-}ØCO_2^{-}\text{-}ØCO_2H]^{*} \xrightarrow{k_7} AH^{+} + ØCO_2^{-} + ØCO_2H + h\nu$$

The scheme takes account of a) the absence of a kinetic isotope effect on reaction rate, b) the existence of an isotope effect on excitation quantum yield, and c) the pK-value difference between chemiluminescence and acridine fluorescence. Because of c), a secondary transition complex located in a potential well between reactants and products must be postulated. This complex is denoted by $[AH^{+}\text{-}ØCO_2^{-}\text{-}ØCO_2H]$. It differs from the free acridinium cation by its pK-value and its life time. However, its emission spectrum is identical with that of the free ion. The life time of the electronically excited transition complex can be calculated if the quenching reaction with chloride ion is assumed to be diffusion controlled ($1o^{1o}$ $\text{lmole}^{-1}\text{sec}^{-1}$). It turns out to be $1\text{x}1o^{-8}$ sec at 45° C as compared to $3.2\text{x}1o^{-8}$ sec for the acridinium cation in 1 N H_2SO_4 at 2o° C (2).

In the scheme presented the excitation quantum yield is defined by $k_4/(k_3+k_4)$ and the emission yield by $k_7/(k_6+k_7)$.

It should be noted that the absence of an N-D isotope effect on excitation quantum yield is in agreement with the tight binding of the N-hydrogen within the transition complex as expressed by its large pK_a as compared to acridine.

The fact that the total quantum yield of the reaction in PrOD-D_2O exceeds that in PrOH-H_2O by a factor of 1.3 can be explained by the higher emission yield of protonated acridine in the more viscous PrOD-D_2O.

In order to test the mechanism proposed the dependence of the reaction rate on the electron density of the N of AH_2 and the -O-O- of DBP is being investigated.

EXPERIMENTAL

9.9'-dideuteroacridan was prepared by reduction of acridone with sodium in monodeutero-1-butanol (OD) (3). The product was recrystallized from ethanol and identified by nmr-spectroscopy. The isotopic purity was found to be better than 95%. The absolute sensitivity of the chemiluminescence apparatus was determined using the method of Hastings and Weber (4).

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