

EQUILIBRIUM pK^* OF CARBAZOLE STUDIED BY THE DEPROTONATION REACTION IN AMMONIACAL AQUEOUS MEDIA

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Summary

Forward and backward rate constants for the excited state deprotonation reaction of carbazole in ammoniacal aqueous media were determined from both steady state (Weller's fluorescence quenching technique) and direct kinetic studies. The results establish that the equilibrium pK^* may be significantly different from the "apparent" pK^* obtained by the fluorometric titration method.

1. Introduction

It is a well-established fact that there is a marked change in the ionization constants of organic acids and bases when they are excited to higher electronic states [1 - 9]. Steady state titrimetric studies give an estimate of the pK^* values of acids or bases, but these do not always correspond to the equilibrium pK^* [10, 11]. It is the latter quantity which should be correlated with the charge density or any other property calculated for the molecule. The apparent pK^* will change if the lifetime of the excited state is altered on the addition of quenchers. This anomaly results from the transitory character of the excited species, which does not always allow equilibrium to be reached. A cursory look at the apparent pK^* obtained by the fluorometric titration method shows that, despite large differences in molecular structure and acid-base properties in the ground state, almost all amines have pK^* around 12 for the deprotonation reaction [6]. One wonders why. A little reflection will, however, show that if the equilibrium pK^* is much less than 12, say 8, even the diffusion-controlled deprotonation rate (with a rate constant of about $10^{10} \text{ M}^{-1} \text{ s}^{-1}$) at pH 8, 9 or 10 will be much slower than the rate of decay of the excited species, and the production of the deprotonated form will thus be insignificant. The overall consequence of the transitory character of the species will be that in fluorometric titrations the deprotonated form will not be detected till a pH of 11 or 12 is reached.

Our long term goal is to relate the acid–base character of the excited state to the calculated molecular properties of the state. To do so, we need the equilibrium pK^* . This can be obtained either by the Förster cycle method if the ground state pK is known or by measurement of the forward and the backward rate constants. The latter, in turn, can be obtained by either Weller's fluorescence quenching method or direct kinetic measurements [2, 11 - 19]. The problems associated with the Förster cycle method have been discussed by a number of workers [12, 13]. Besides, the ground state pK value for the deprotonation process is not measurable in this case. We have therefore adopted the straightforward technique, namely we have determined the steady state quenching constant and performed direct time-resolved measurements; the equilibrium constant was found from the ratio of the forward and backward rate constants. In a previous communication [2], we showed that the true pK^* of carbazole is one unit lower than the reported apparent pK^* . On closer scrutiny, we found that the reverse reaction rate of



was much too small, compared with the on-going competing other fast processes, to be determined with any accuracy at all, and the determined pK^* gives only an upper limit. Furthermore, the concentration of H_2O could not be varied to find out the dependence of the reverse rate on the concentration of the reacting species. We have, therefore, searched for an alternative acid–base reaction where the reverse reaction rate is appreciable compared with the forward reaction rate and, moreover, can be changed systematically by the addition of the acid form of the added base. In this paper, we discuss the proton transfer reaction with ammonia and show that the equilibrium pK^* of carbazole is as low as 7.58 ± 0.3 .

2. Experimental details

Carbazole was purified as described previously [2]. Triply distilled water was used for the preparation of solutions. Ammonium hydroxide and ammonium chloride (both Ranbaxy analytical reagents) were used without further purification. For the kinetic experiments, the solutions were not degassed since it was verified that the dissolved gases had no effect on the lifetime of the excited species.

A Cary 17D spectrophotometer and a Perkin–Elmer MPF 44B spectrofluorometer were used for recording absorption spectra and emission spectra respectively. For time-resolved fluorescence decay measurements, the time-correlated single-photon-counting technique was adopted. The instrumentation has been described elsewhere [2]; the only difference in this work was that the exciting pulses were generated from a nitrogen-filled 200 kHz nanosecond flash lamp (Applied Photophysics) instead of the argon ion laser pumped dye laser used previously.

3. Results and discussion

The fact that the luminescence of the anion exceeds that of the neutral carbazole, in the presence of 1:1 $\text{NH}_4\text{OH}:\text{NH}_4\text{Cl}$ buffer (concentration, at least 0.7 N) means that the $\text{p}K^*$ has to be less than 9.25, even if we assume that the deprotonation and the reverse protonation rates are sufficiently fast (compared with the lifetimes of the excited species involved) for the equilibrium to be established. With the highest concentration of 1:1 buffer used, the reverse rate is an order of magnitude less than the lifetime of the anion; this means that the equilibrium $\text{p}K^*$ should be appreciably less than 9.25. In fact, a weak base such as triethanolamine ($\text{p}K_a = 7.76$) [20] generates the carbazole anion in the excited state, indicating that the $\text{p}K^*$ could be as low as 7.76.

3.1. Mechanism

The mechanism adopted for a quantitative discussion of the data is given in Fig. 1. AH and A^- represent carbazole and its anion respectively, and all the rate constants are denoted by their usual symbols.

3.2. Intensity quenching on excitation by a steady light source

The variation in the carbazole luminescence intensity with added ammonia is shown in Fig. 2. As the ammonia concentration increases, the intensity of the 360 nm band gradually diminishes and the 415 nm band characteristic of the deprotonated form [11] grows in. No change in the absorption spectrum was observed. By applying the Stern-Volmer equation,

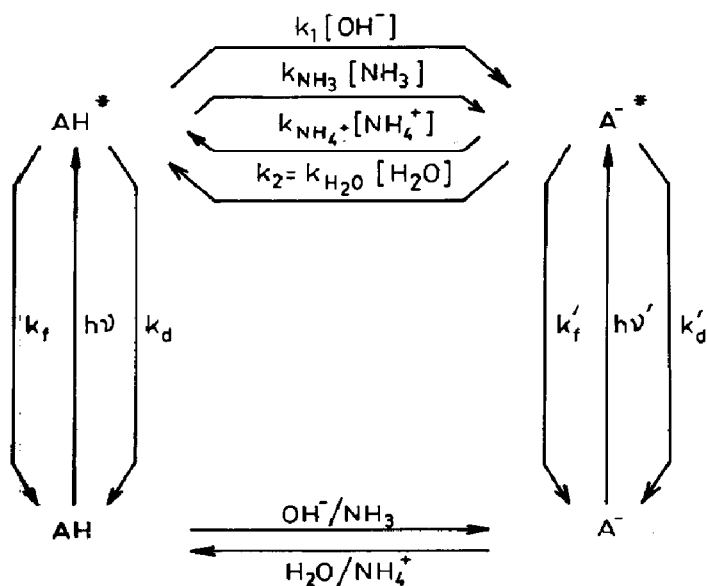


Fig. 1. Kinetic scheme for the proton transfer reaction of carbazole in the ground and the excited states.

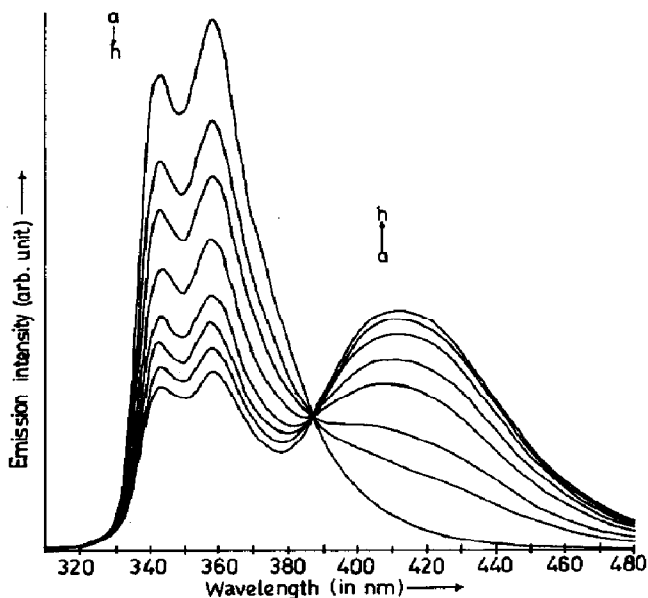


Fig. 2. Fluorescence spectra of carbazole at different ammonia concentrations. The different ammonia concentrations in spectra a - h are 0.0 M, 0.05 M, 0.1 M, 0.2 M, 0.3 M, 0.4 M, 0.5 M and 0.6 M respectively. The excitation wavelength was 295 nm.

TABLE 1

Rate constants and pK^* derived from the steady state and the time-resolved studies

Rate constants	Steady state	Time resolved
$k_f + k_d$	—	9.50×10^7
$k_f' + k_d'$	—	4.50×10^7
k_{NH_3} (using NH_4OH)		
Uncorrected for OH^- contribution	3.00×10^8	3.74×10^8
Corrected for OH^- contribution	2.66×10^8	3.35×10^8
Using NH_4OH-NH_4Cl buffer	2.82×10^8	2.99×10^8
$k_{NH_3^+}$		
Using concentration units	5.27×10^6	4.33×10^6
Using activities ^a	8.72×10^6	7.20×10^6
pK^*		
In concentration units	7.50	7.44
In activity units	7.74	7.63

^aFor the activity correction the Debye-Hückel equation was employed.

k_{NH_3} was evaluated from the decrease in intensity of the 360 nm band. The OH^- ion concentration is proportional to the square root of the concentration of ammonia. Since the forward rate constant k_1 is known from our previous experiment [2], the contribution of OH^- ions to the quenching can be calculated. This was found to be of little significance; nevertheless, the data were corrected for it. The value of k_{NH_3} is given in Table 1.

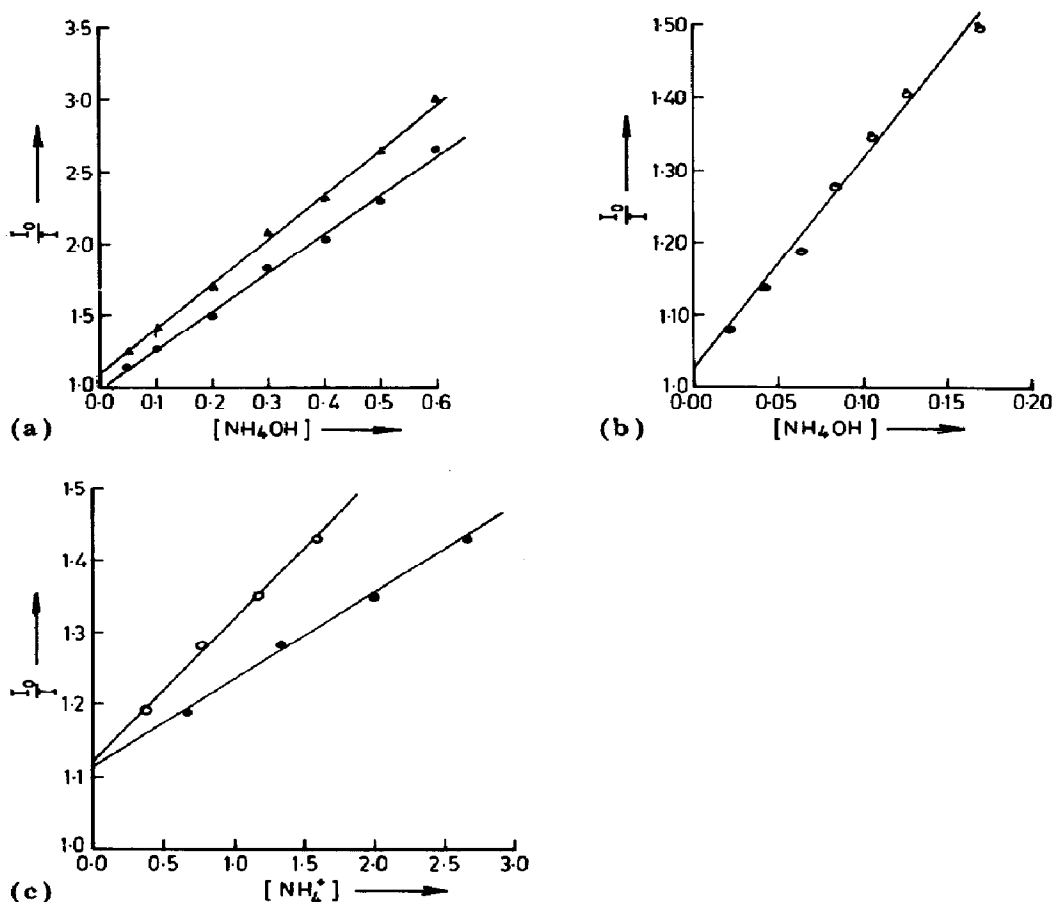


Fig. 3. (a) Plot of I_0/I vs. $[\text{NH}_4\text{OH}]$ (in the absence of NH_4Cl). ▲, uncorrected; ●, corrected for OH^- contribution. (b) Plot of I_0/I vs. $[\text{NH}_4\text{OH}]$ (1:1 $\text{NH}_4\text{OH}:\text{NH}_4\text{Cl}$ buffer added). ●, uncorrected; ○, corrected for Cl^- quenching. (c) Plot of I_0/I vs. $[\text{NH}_4^+]$ (concentration of NH_3 , 0.17 M). ●, in concentration units; ○, in activity units.

In another set of experiments the absolute concentration of dilute 1:1 $\text{NH}_4\text{OH}:\text{NH}_4\text{Cl}$ buffer was varied. The buffer keeps the OH^- ion concentration small and almost constant, but introduces two new ions, NH_4^+ and Cl^- . Using NaCl it was verified that Cl^- ion at the concentrations used in these experiments does not cause any appreciable quenching. The correction for Cl^- quenching is shown in Fig. 3(b). The NH_4^+ ion does influence the backward rate, but the backward rate is much slower than the forward one (see Table 1). The rate constant k_{NH_3} obtained from the Stern-Volmer plot after correction for the influence of NH_4^+ ion is given in Table 1.

The backward rate constant $k_{\text{NH}_4^+}$ was determined by varying the concentration of NH_4^+ ion but keeping the concentration of NH_3 constant. As the NH_4^+ ion concentration increases the 415 nm band decreases and the 360 nm band increases in intensity. $k_{\text{NH}_4^+}$ was evaluated using the same Stern-Volmer equation by monitoring the anion luminescence. Figure 3 shows plots of the steady state experimental data.

3.3. Direct kinetic measurements

The kinetic scheme depicted in Fig. 1 leads to the following differential equations:

$$-\frac{d[\text{AH}^*]}{dt} = (k_f + k_d + k_1[\text{OH}^-] + k_{\text{NH}_3}[\text{NH}_3])[\text{AH}^*] - (k_2 + k_{\text{NH}_4^+}[\text{NH}_4^+])[\text{A}^{-*}] \quad (1)$$

and

$$-\frac{d[\text{A}^{-*}]}{dt} = (k_f' + k_d' + k_2 + k_{\text{NH}_4^+}[\text{NH}_4^+])[\text{A}^{-*}] - (k_1[\text{OH}^-] + k_{\text{NH}_3}[\text{NH}_3])[\text{AH}^*] \quad (2)$$

Using the boundary conditions

$$[\text{AH}^*]_{t=0} = [\text{AH}^*]_0 \quad [\text{A}^{-*}]_{t=0} = 0$$

and substituting X , Y , m_1 and m_2 for $(k_f + k_d + k_1[\text{OH}^-] + k_{\text{NH}_3}[\text{NH}_3])$, $(k_f' + k_d' + k_2 + k_{\text{NH}_4^+}[\text{NH}_4^+])$, $(k_2 + k_{\text{NH}_4^+}[\text{NH}_4^+])$ and $(k_1[\text{OH}^-] + k_{\text{NH}_3}[\text{NH}_3])$ respectively, we get

$$[\text{AH}^*]_t = \frac{[\text{AH}^*]_0}{\lambda_1 - \lambda_2} \{(X - \lambda_2) \exp(-\lambda_1 t) + (\lambda_1 - X) \exp(-\lambda_2 t)\}$$

and

$$[\text{A}^{-*}]_t = \frac{(k_1[\text{OH}^-] + k_{\text{NH}_3}[\text{NH}_3])[\text{AH}^*]_0}{\lambda_2 - \lambda_1} \{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\}$$

Here, $\lambda_1 = \tau_1^{-1}$ and $\lambda_2 = \tau_2^{-1}$, τ_1 and τ_2 being the two lifetimes (experimental quantities) of the neutral species and the anionic species respectively;

$$\begin{aligned} \lambda_1, \lambda_2 &= \tau_1^{-1}, \tau_2^{-1} \\ &= \frac{1}{2} [(X + Y) \pm \{(X + Y)^2 - 4(XY - m_1 m_2)\}^{1/2}] \end{aligned}$$

The scheme shows that the emission of both the neutral and the anionic forms should follow a double-exponential decay. The neutral form, however, shows a single-exponential decay while the decay of the anion is double exponential. This deviation for the former is due to the very low value of the pre-exponential factor for the longer component [17].

For the kinetic determination of k_{NH_3} and $k_{\text{NH}_4^+}$, we used the following equation:

$$\begin{aligned} \lambda_1 + \lambda_2 &= X + Y \\ &= (k_f + k_d + k_f' + k_d' + k_1[\text{OH}^-] + k_{\text{NH}_4^+}[\text{NH}_4^+] + k_2) \\ &\quad + k_{\text{NH}_3}[\text{NH}_3] \end{aligned} \quad (3)$$

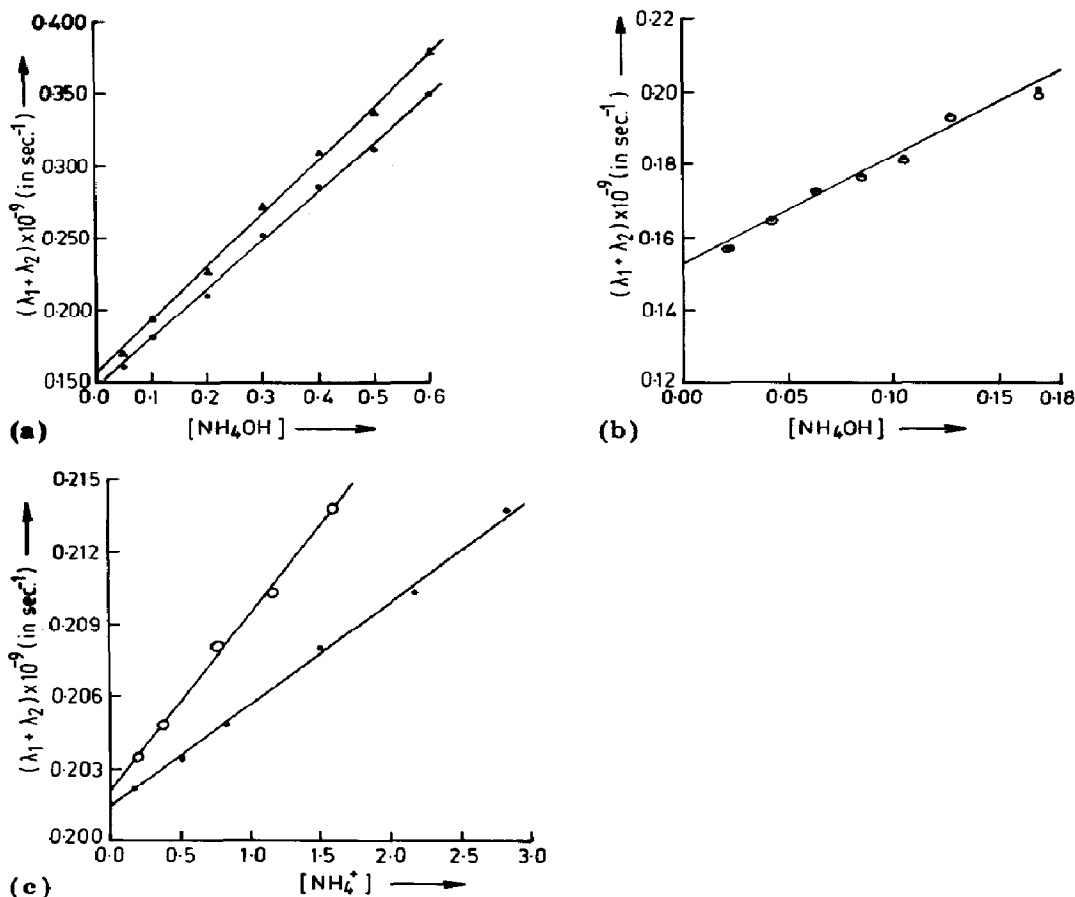


Fig. 4. (a) Plot of $\lambda_1 + \lambda_2$ vs. $[\text{NH}_4\text{OH}]$ (in the absence of NH_4Cl). \blacktriangle , uncorrected; \bullet , corrected for OH^- contribution. (b) Plot of $\lambda_1 + \lambda_2$ vs. $[\text{NH}_4\text{OH}]$ (1:1 $\text{NH}_4\text{OH}:\text{NH}_4\text{Cl}$ buffer added). \bullet , uncorrected; \circ , corrected for Cl^- quenching. (c) Plot of $\lambda_1 + \lambda_2$ vs. $[\text{NH}_4^+]$ (concentration of NH_3 , 0.17 M). \bullet , in concentration units; \circ , in activity units.

$$= (k_f + k_d + k_f' + k_d' + k_1[\text{OH}^-] + k_2 + k_{\text{NH}_3}[\text{NH}_3]) + k_{\text{NH}_4^+}[\text{NH}_4^+] \quad (4)$$

The slope of the plot of $\lambda_1 + \lambda_2$ against NH_3 concentration, at a fixed NH_4^+ ion concentration, gives k_{NH_3} . The observed data were corrected for the change in the OH^- contribution when the experiment was done in the absence of NH_4Cl . In another experiment, the buffer concentration but not the ratio was varied. The correction for the NH_4^+ ion variation, fortunately, turns out to be negligible. The correction due to Cl^- ion is shown in Fig. 4(b).

Similarly, from eqn. (4), at a fixed NH_3 concentration the slope of the plot of $\lambda_1 + \lambda_2$ vs. NH_4^+ ion concentration gives $k_{\text{NH}_4^+}$. Here also, the correction due to OH^- variation was found to be negligible. The plots for the kinetic experiments are shown in Fig. 4.

The observed rate constants, from both steady state and kinetic methods, are given in Table 1.

It should be pointed out that our kinetic measurements have been made under conditions away from equilibrium and hence the equilibrium constant calculated from the kinetic constants may be slightly different from the true equilibrium value. In our kinetic expressions and hence in the final calculated equilibrium constant, concentrations appear instead of activities; although we have recalculated the $k_{\text{NH}_4^+}$ using activities in the kinetic expression, the $\text{p}K^*$ may be a bit off from the true thermodynamic $\text{p}K^*$. Taking into account the other sources of error, we estimate that the reported $\text{p}K^*$ value is correct only to within ± 0.3 units.

It should be pointed out that the backward and forward rates are much less than the diffusion-controlled value; this means that there is an activation barrier for the processes. The determination of the activation energies and their correlation with the $\text{p}K$ values of the bases is in progress [9].

Another point of interest is the correlation of the deprotonation $\text{p}K^*$ with the charge densities on the nitrogen atom for a series of carbazole derivatives. Such correlations have been established for the ground state of pyridine and the pyrazine protonation reaction, but no such systematization is yet available for the excited state. We are presently determining the $\text{p}K^*$ of a number of carbazole derivatives with a view to establishing such a correlation.

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