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IONIZATION KINETICS OF RHODAMINE B LEUCOCYANIDE IN THE PRESENCE OF POLY(VINYLBENZYLTRIMETHYLAMMONIUM CHLORIDE)

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The participation of the carboxylate group in the ionization of Rhodamine B leucocyanide was studied in an aqueous solution of poly(vinylbenzyltrimethylammonium chloride) (PVBTA) or cetyltrimethylammonium bromide (CTAB) at constant temperature and pH 8. The experimental rate constant (k_{exp}) decreases with increasing PVBTA concentration. The results are interpreted in terms of the binding of the ionized form of Rhodamine B leucocyanide ($RBCN^-$) to a single class of completely independent binding sites on the PVBTA. From this model, a value of $1{\cdot}09 \times 10^6$ l mol^{-1} was obtained for the binding constant. The effect of CTAB is different from that obtained with PVBTA. After a region in which there are large changes in k_{exp} with the CTAB concentration, this constant reaches a zone where its value is independent of the surfactant concentration. The decrease in k_{exp} in the first zone was explained in terms of an ionic association between $RBCN^-$ and the cationic heads. In the second zone, it was assumed that a micellar effect operates on the ionization kinetics. In a similar form, the esterification of the carboxylate group leads to a slower ionization rate.

INTRODUCTION

The triphenylmethane leucocyanide dyes are readily prepared from an aqueous solution of potassium cyanide and the basic dye at room temperature. They are stable and revert to the parent dye only by photochemical reactions.[1] On the other hand, Rhodamine B leucocyanide has been found to have a remarkably reactive nitrile group, in strong contrast to the behaviour of the familiar triphenylmethane dye cyanides.[2] In aqueous solutions it rapidly reverts to the parent dye and potassium cyanide.

In previous work,[3] we studied the effect of temperature and pH on the ionization kinetics of Rhodamine B leucocyanide to Rhodamine B and cyanide in aqueous solution. This reaction follows a first-order rate law and the experimental rate constant (k_{exp}) was affected by the hydrogen ion concentration. At constant temperature, k_{exp} increases with increasing pH and its value reaches a plateau at pH 7.

The effect of pH on the experimental rate constant could be explained if protonation of the carboxylic group changes the reactivity of the leucocyanide dye. Taking into account this model, the acid dissociation constant of the carboxylic group of Rhodamine B leucocyanide was obtained as 2×10^{-6} M. Therefore, at pH > 7 the ionized form of Rhodamine B leucocyanide ($RBCN^-$) is preponderant, so k_{exp} is independent of pH and the ionization reaction can be represented by the chemical equation shown in Figure 1.

These results suggested the possibility that the carboxylate group is assisting the elimination of the cyanide ion from $RBCN^-$. The intramolecular participation of the carboxylate group can be seen either as a nucleophilic assistance (the neighbouring group mechanism or anchimeric assistance[4,5]) or an electrostatic stabilization of a developing carbonium ion in the transition state.[6]

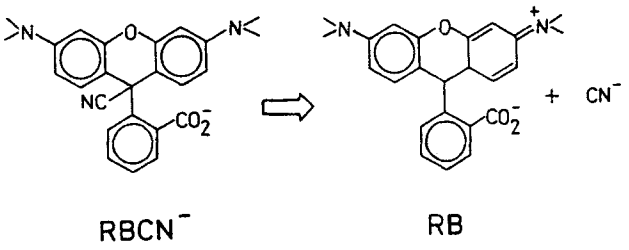

Figure 1. Ionization reaction of Rhodamine B leucocyanide

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In this paper we present evidence of this intramolecular participation from experiments involving the addition of polyelectrolytes and surfactants to the reaction system and by the esterification of the carboxylate group. These experiments lead to a slower decomposition rate of $RBCN^-$, supporting the participation of the carboxylate group in the elimination of the cyanide ion from $RBCN^-$.

EXPERIMENTAL

$RBCN^-$ was prepared from Rhodamine B hydrochloride (Merck) and potassium cyanide (Carlo Erba). The method was similar to that employed by Chalkley.[2] Rhodamine 6G leucocyanide was prepared from Rhodamine 6G hydrochloride (Merck) in a similar way.

A stock solution of Rhodamine B leucocyanide was prepared in dimethyl sulphoxide (Merck) because in this solvent the decomposition rate is very slow at room temperature. An aliquot, to give a final concentration of $RBCN^-$ about 1×10^{-5} M was added to a Tris (Sigma Chemical) buffer solution of 10^{-3} M (pH 8). This solution contained a selected concentration of cetyltrimethylammonium bromide (CTAB) (BDH) or poly(vinlybenzyltrimethylammonium chloride) (PVBTA) (molecular weight 300 000; Dow Chemical). The reaction rates were followed with a Hewlett-Packard Model 8452A diode-array spectrophotometer in double-walled, thermostated UV absorption cells, measuring the production of RB at 554 nm.[7] The experimental first-order rate constants (k_{exp}) were obtained from plots of $\log(A_\infty - A_t)$ vs time. In all the experiments, A_∞ was obtained by heating the reaction solution at 90 °C for several hours, then cooling to the working temperature and reading the absorbance.

Sodium chloride (Merck) and urea (BDH) were used as received. Water was triply distilled.

RESULTS AND DISCUSSION

In aqueous solution, PVBTA is a strong polyelectrolyte that dissociates to a polycation and chloride ions. Its ionization is not affected by pH. In order to study the ionization of Rhodamine B leucocyanide in the presence of PVBTA, we worked at pH 8. At this pH, the ionized form of Rhodamine B cyanide prevails and the experimental rate constant is therefore independent of pH. The ionization reaction is shown in Figure 1.

The visible absorption band and the molar absorptivity of Rhodamine B were unaffected by the presence of PVBTA. Therefore, the effect of PVBTA on the ionization kinetics was followed by measuring the absorbance of the RB vs time. In the presence of PVBTA this reaction also follows a first-order rate law.

The presence of PVBTA in aqueous solution of $RBCN^-$ at constant pH and temperature produced a strong decrease in k_{exp}. A plot of k_{exp} in the presence of PVBTA as a function of polyelectrolyte concentration in equivalents per litre is given in Figure 2. It shows, within the PVBTA concentration range tested, two zones with very different dependences on the polymer concentration, one with a steep slope at low PVBTA concentrations and the other with a small slope at higher concentrations.

The behaviour of the experimental rate constant for the decomposition of $RBCN^-$ in the presence of PVBTA is very similar to the spectrophotometric behaviour of cationic dyes in the presence of anionic polyelectrolytes found in other studies.[8,9] In these papers a spectrophotometric method of determining anionic sites on polymers by titration with basic dyes was proposed, assuming that the maximum aggregation (corresponding to minimum absorbance of the dye monomer) occurs at a 1 : 1 ratio between anionic sites and dye molecules.

In order to explore whether the observed changes in the ionization rates of Rhodamine B leucocyanide with the addition of PVBTA is a true polyelectrolyte effect or a solvent effect, we investigated the influence of the solvent on the reaction rate. We carried out experiments in water–dioxane, water–ethanol and water–formamide mixtures. In the first solvent mixture, as in dimethyl sulphoxide, the reaction rate is too slow to be observed. With the other mixtures, k_{exp} increases slightly with increase in solvent polarity.[4] The results are presented as relative rates in Table 1.

The observed effect of solvent polarity on the ionization reaction is smaller than the polyelectrolyte effect

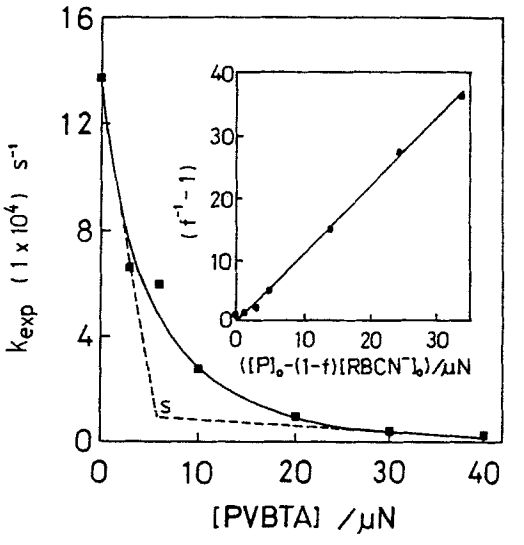

Figure 2. Plot of k_{exp} in the presence of PVBTA at pH 8 and 60 °C. $[RBCN^-] = 7\ \mu M$. Point S denotes the stoichiometric relationship between PVBTA and $RBCN^-$. Inset: plot of the data according to equation (5).

Table 1. Solvent effect on the experimental rate constant in mixtures of an organic solvent and water at 41 °C, presented as values relative to the rate constant in water ($8{\cdot}8 \times 10^{-5}$ s^{-1})

Organic solvent	Concentration (%, v/v)	k_{rel}
Ethanol	10	0·918
	20	0·667
Formamide	10	1·16
	20	1·25

mentioned above. Therefore, the large decrease in k_{exp} in the presence of PVBTA cannot be explained only by the effect of polarity on the ionization reaction. Hence we should consider how the specific interaction between PVBTA and the $RBCN^-$ affects the reaction rate.

The point at which the ratio of cationic sites on the polyelectrolyte to $RBCN^-$ is approximately unity constitutes a characteristic point of the system. At this point the amounts of $RBCN^-$ (moles) and PVBTA (equivalents) correspond approximately to the stoichiometric relationship (see point S in Figure 2).

From all these indications we considered the PVBTA–$RBCN^-$ interaction in terms of the binding to a single class of completely independent binding sites.[10] The development of this model can be expressed by the following equations:

$$P + RBCN_f^- \rightleftharpoons RBCN_b^- \quad (1)$$

$$K_b = \frac{(RBCN_b^-)}{[RBCN_f^-]([P]_0 - [RBCN_b^-])} \quad (2)$$

where $[RBCN_b^-]$, $([P]_0 - [RBCN_b^-])$ and $[P]_0$ are the concentrations of occupied binding sites, unoccupied binding sites and total PVBTA, respectively, $[RBCN_f^-]$ is the concentration of free Rhodamine B leucocyanide in water and K_b is the binding constant. Further, it was assumed that the number of binding sites on the polyelectrolyte is equal to the number of ionized groups.

If it is assumed that only the free Rhodamine B leucocyanide is able to decompose, the experimental rate constant of ionization of the $RBCN^-$ could be expressed by

$$d[RB]/dt = k_{exp}[RBCN^-]_0 = k[RBCN_f^-] \quad (3)$$

where $[RBCN^-]_0$ is the total concentration of $RBCN^-$ and k corresponds to the rate constant of free $RBCN^-$ in water ($1{\cdot}37 \times 10^{-3}$ s^{-1} at 60 °C).

From equations (2) and (3) we obtain

$$k/k_{exp} = [RBCN^-]_0/[RBCN_f^-] = f^{-1} = 1 + K_b([P]_0 - [RBCN_b^-]) \quad (4)$$

$$f^{-1} - 1 = K_b\{[P]_0 - (1-f)[RBCN^-]_0\} \quad (5)$$

where f is the fraction of free $RBCN^-$ or unbound to PVBTA.

The representation of the data according to equation (5) gives a linear plot from which K_b can be evaluated (see Figure 2, inset). A value of $(1{\cdot}09 \pm 0{\cdot}02) \times 10^6$ l mol^{-1} was obtained, which is comparable to the binding constants found for the interaction of dyes with polyelectrolytes.[11,12] K_b was also measured by a spectrophotometric method at 30 °C, the highest temperature compatible with $RBCN^-$ stability. An equilibrium constant of $(0{\cdot}8 \pm 0{\cdot}1) \times 10^6$ l mol^{-1} between $RBCN^-$ and the polyelectrolyte was obtained from difference spectra employing the Rose–Drago procedure,[13] followed by a non-linear regression data analysis program. This result was in close agreement with that obtained by the kinetic method.

The addition of sodium chloride to a solution of $RBCN^-$ containing PVBTA increases the value of k_{exp}. The results are presented as values relative to k_{exp} in water in Figure 3. This effect can be explained if the $RBCN^-$ becomes excluded from the polymer domains when the concentration of sodium chloride is increased.[14,15] This happens because the shielding of the potential field of the polyion domains by the Cl^- ions reduces the electrostatic attraction for the $RBCN^-$. The sodium chloride effect tends to reverse the polyelectrolyte effect on k_{exp} but the observed reversion is partial, and turns out to be only about 60%. This suggests that the interaction of $RBCN^-$ with the site binding on PVBTA must be explained in terms of electrostatic and hydrophobic forces.

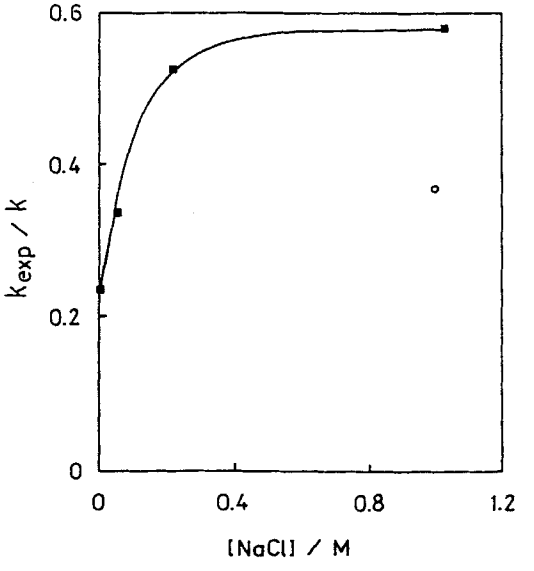

Figure 3. Effect of (■) sodium chloride and (○) urea on k_{exp} in a 10 μM aqueous solution of PVBTA at pH 8 and 60 °C. $[RBCN^-] = 7$ μM. The results are presented relative to the rate constant in water

Similarly, k_{exp} in an aqueous PVBTA solution also increases in the presence of urea (see Figure 3). This may be because of the decrease in the hydrophobic interactions caused by the addition of urea.[16] The reversion of the polyelectrolyte effect on k_{exp} by 1 M urea is about 40%.

Finally, both sets of experimental results suggest that the decrease in the rate of ionization of $RBCN^-$ by PVBTA is the result of electrostatic and hydrophobic binding of Rhodamine B leucocyanide to the polyelectrolyte. A similar interpretation was given for the binding of eosin Y to synthetic polymers.[17]

On the other hand, the presence of CTAB (a cationic surfactant) in aqueous solutions of Rhodamine B leucocyanide also produces a decrease in k_{exp} (Figure 4). The results are presented as the logarithm of the values relative to the rate constant in water ($2{\cdot}8 \times 10^{-4}$ s^{-1} at 50 °C). Figure 4 shows two zones, as with PVBTA. However, there are important differences. In the region of large slopes, the amount of surfactant necessary to obtain a similar decrease in the rate constant is at least five times larger than the amount of PVBTA. In the other zone, the experimental rate constant is independent of the surfactant concentration. This region starts at a CTAB concentration smaller than the critical micellar concentration (cmc) in water (0·9 mM).[18] It is known that the addition of dyes[19] and other ionic solutes of opposite charge to the detergent[20] induces the formation of micelles or premicelles. This effect can be observed in Figure 4, where an operational cmc of about 0·2 mM can be estimated.

The results in the presence of CTAB can be explained by the assumption that an ionic association between the $RBCN^-$ and the cationic heads of the surfactant is present in the first zone. The existence of true ion-association complexes formed at below the cmc between ionic surfactants and dyes with opposite charge is supported by most of the published data. These complexes are electrically neutral, and often are poorly soluble in water but readily extracted by low-polarity solvents. They have stoichiometric surfactant/dye ratios. At surfactant concentrations at the cmc value and above, the solubilizing effect of the micelles begins to be important and the ion-association complexes are incorporated into the micelles.[19]

The second region is that where aggregates of surfactant molecules are present in the form of micelles or premicelles and the ion pairs are solubilized there. In this region it can be considered that all the Rhodamine B leucocyanide is associated with the surfactant and is reacting as dissolved in a solvent of lower polarity.

In another experiment we studied the effect of the esterification of the carboxylate group on k_{exp}. The reactivity of Rhodamine 6G leucocyanide (where the carboxylate group is esterified) was compared with Rhodamine B leucocyanide. The comparison was made

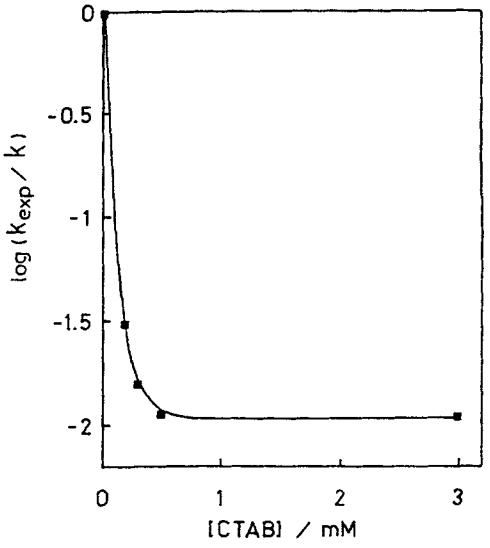

Figure 4. Effect of CTAB on k_{exp} at pH 8 and 50 °C. $[RBCN^-] = 7$ μM. The results are presented as the logarithm of the values relative to the rate constant in water ($2{\cdot}8 \times 10^{-4}$ s^{-1})

in 10% (v/v) ethanol–water containing 10^{-3} M Tris because Rhodamine 6G leucocyanide is not an ionic compound and does not bind electrostatically to PVBTA. The rate constant for the ionization of Rhodamine 6G leucocyanide is lower than that of Rhodamine B leucocyanide by a factor of 2·5. This result suggests that the ester group also assists the elimination of cyanide ion but to a lesser extent than the carboxylate group. It is known[4] that the ester group is one of the more important neighbouring groups with unshared electrons.

From the above results, the large decrease in k_{exp} in the presence of CTAB or PVBTA cannot be explained simply by the formation of ion pairs between $RBCN^-$ and the trimethylammonium cationic heads of CTAB and PBVTA. For example, in the system $RBCN^-$–PVBTA we showed that the decrease in the ionization rate is the result of electrostatic and hydrophobic binding of $RBCN^-$ to the polyelectrolyte. Moreover, that binding cannot only change the properties of $RBCN^-$ but also affects the macromolecular characteristics of the PVBTA, producing conformational changes and altering the microenvironment where the reaction is carried out.

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REFERENCES

1. (a) L. Harris and J. Kaminski, *J. Am. Chem. Soc.* **57**, 1154–1159 (1935); (b) J. G. Calvert and H. J. L. Rechen, *J. Am. Chem. Soc.* **74**, 2101 (1952); (c) M. L. Herz, *J. Am. Chem. Soc.* **97**, 6777–6785 (1975); (d) R. G. Brown and J. J. Cosa, *Chem. Phys. Lett.* **45**, 429–431 (1977); (e) J. J. Cosa and H. E. Gsponer, *J. Photochem. Photobiol. A: Chem.* **48**, 303–311 (1989).
2. L. Chalkley, *J. Org. Chem.* **26**, 408–412 (1961).
3. J. J. Cosa, H. Menez and H. E. Gsponer, *An. Asoc. Quim. Argen.* **69**, 349–355 (1981).
4. J. March, *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, McGraw-Hill, New York (1968).
5. E. Anderson and B. Capon, *J. Chem. Soc., Perkin Trans. 2* 515–522 (1972).
6. B. M. Dunn and T. C. Bruice, *J. Am. Chem. Soc.* **92**, 6589–6594 (1970); **93**, 5725–5731 (1971).
7. R. W. Ramette and E. B. Sandell, *J. Am. Chem. Soc.* **78**, 4872–4878 (1956).
8. V. Vitagliano and L. Costantino, *J. Phys. Chem.* **74**, 197–202 (1970).
9. V. Vitagliano, L. Costantino and A. Zagari, *J. Phys. Chem.* **77**, 204–210 (1973).
10. C. Tanford, *Physical Chemistry of Macromolecules*. Wiley, New York (1961).
11. R. B. Cundall, J. B. Lawton, D. Murray and G. O. Phillips, *J. Chem. Soc., Perkin Trans 2* 879–884 (1979).
12. M. Mandel and W. H. J. Stork, *Biophys. Chem.* **2**, 137–143 (1974).
13. R. Foster, *Organic Charge-Transfer Complexes*. Academic Press, New York (1969).
14. Y. Kurimura, H. Yokota, K. Shigehara and E. Tsuchida, *Bull. Chem. Soc. Jpn.* **55**, 55–58 (1982).
15. E. Baumgartner, S. G. Bertolotti, J. J. Cosa, H. E. Gsponer, M. Hamity and C. M. Previtali, *J. Colloid. Interface Sci.* **115**, 417–421 (1987).
16. N. Muller, *J. Phys. Chem.* **94**, 3856–3859 (1990).
17. G. R. Jones, R. B. Cundall, D. Murray and D. A. Duddell, *J. Chem. Soc., Faraday Trans 2* **80**, 1201–1213 (1984).
18. J. H. Fendler, *Membrane Mimetic Chemistry*. Wiley–Interscience, New York (1982).
19. M. E. Diaz Garcia and A. Sanz-Medel, *Talanta* **33**, 255–264 (1986).
20. (a) S. G. Bertolotti, O. E. Zimerman, J. J. Cosa and C. M. Previtali, *Bol. Soc. Chil. Quím*, **35**, 25–31 (1990); (b) S. G. Bertolotti, N. A. García and H. E. Gsponer, *J. Colloid Interface Sci.* **129**, 406–413 (1989); (c) S. G. Bertolotti, O. E. Zimerman, J. J. Cosa and C. M. Previtali, *J. Lumin.* (submitted for publication).