J. Chem. Research (S), 1997, 326–327†

Kinetic and Spectroscopic Evidence for the Formation of Ion-pairs between Crystal Violet and Perchlorate Ion†

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Kinetic data for the inhibition of the reaction between Crystal Violet (CV) and hydroxide ions by perchlorate ions are used to determine the equilibrium constant for the formation of ClO_4–CV ion-pairs; K is obtained as 110 ± 14 dm^3 mol^{-1} at 25 °C and ionic strength (I) = 0 mol dm^{-3}.

Crystal Violet (CV) is a carbonium ion that is stabilized by the presence of aromatic rings which give it strong resonance that results in a deep blue-violet colour with an absorption maximum in the visible region ($\lambda_{max} = 590$ nm).

The CV cation occurs as two helicoidal isomers[1] owing to the strong steric hindrance between the benzene *ortho* protons which lead to a non-planar configuration. The two isomers have the same typical helicoidal structures as carbonium ions possessing three benzene rings.[2] The presence of these two isomers gives rise to two different absorption bands in the visible spectrum at 590 and 540 nm.[1]

The reactivity of this cation is of high physicochemical interest since it was used, together with those of similar cations, for establishing Ritchie's N^+ nucleophilic index. Its reactivity towards the hydroxide ion, which was used in this work as a kinetic probe to determine the formation constant for the ion-pair, has been widely studied in aqueous solutions[4] and alternative media.[4,5]

This paper contributes experimental evidence for the formation of ion-pairs between the perchlorate ion and Crystal Violet based on spectrophotometric and kinetic data.

We chose the perchlorate ion because its salts are widely used to fix the ionic strength in kinetics studies and because we had earlier found ion-pair complexes between perchlorate ions and nitrogen cations.[7] We did not detect the formation of ion-pairs between CV and other anions such as azide, sulfate or thiocyanate.

Experimental

All chemicals used were of the highest commercially available purity and none required further purification. The experimental procedure employed has been described in detail elsewhere.[6]

Results and Discussion

The spectral behaviour of CV in the presence of perchlorate ions was found to be anomalous as regards the relative heights of the two bands exhibited by the dye. These bands correspond to the absorption of the two helicoidal isomers of CV.[1] The ratio of band A to B for CV, which is proportional to the relative populations of the two isomers, is highly sensitive to the presence of inert electrolyte and polarity changes in the CV environment.

Perchlorate ions cause a strong change in the CV spectrum as regards both the positions of the bands and their relative intensity. The effect is so marked that it is visually apparent in both the hue and colour depth of the CV solution.

Table 1 illustrates the spectral changes caused by variable amounts of sodium perchlorate in terms of the ratio of band A to band B absorption. Such a ratio, which was determined to be 1.48 in aqueous solutions, is markedly changed by high perchlorate ion concentrations. The effect can be so strong as to invert the populations of the two CV isomers leading to a ratio of only 0.84 in the presence of 0.3 M $NaClO_4$. However, the effect cannot be exclusively ascribed to general salt effect factors because, as can be seen from Table 1, A:B remains constant in the presence of similar amounts of NaCl. In other words, the effect is due to the perchlorate ions.

This behaviour confirms a strong association between the perchlorate ion, as a counterion, and the organic cation, with which it is likely to form an ion-pair. The mechanism by which the ratio of CV isomers is changed can be explained if it is assumed that the perchlorate ion preferably forms an ion-pair with the CV isomer in which the positive charge is located over the nitrogen atom ($\lambda_{max} = 540$ nm), and therefore the relative population of the CV isomer with the charge over the carbon atom ($\lambda_{max} = 590$ nm) decreases with the increase in the perchlorate ion concentration. Another anomalous and probably related behaviour was observed in the well-known reaction between CV and OH^- ions, which was strongly inhibited by the addition of perchlorate ions to the medium (Fig. 1). Again, this behaviour cannot be ascri-

Table 1 Influence of the $NaClO_4$ concentration on the height ratio of the spectral bands for Crystal Violet ($\lambda_A = 590$, $\lambda_B = 540$ nm)

$[NaClO_4]$/M	Isomer A: Isomer B	[NaCl]/M	Isomer A: Isomer B
0	1.48	0	1.49
0.0580	1.03	0.0580	1.47
0.1120	0.96	0.1120	1.48
0.1749	0.87	0.1749	1.46
0.2330	0.86	0.2330	1.47
0.2920	0.84	0.2920	1.47

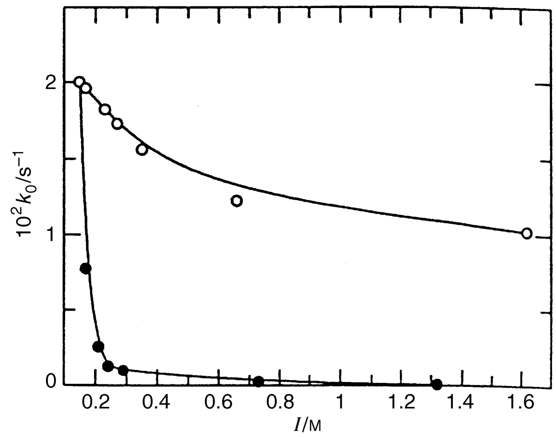

Fig. 1 Inhibitory effect of the presence of sodium perchlorate (●) and sodium chloride (○) in terms of ionic strength on the basic hydrolysis of Crystal Violet. [CV] = 8.33×10^{-6} M; [NaOH] = 0.15 M

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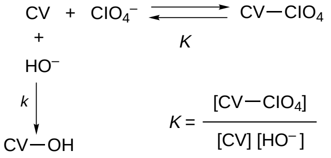
†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.



Scheme 1

bed to a general salt effect since similar concentrations of NaCl resulted in a much weaker inhibition (Fig. 1).

This situation can be interpreted in quantitative terms by assuming that the CV engaged in the formation of the ion-pairs cannot undergo attack by the OH^- ions. Based on Scheme 1, the hydrolysis rate of CV can be described in terms of the amount of free CV in solution, which will be determined by the equilibrium constant for ion-pair formation.

$$v = k[HO^-][CV]_{free} \tag{1}$$

A mass balance for the CV concentration and substitution of its result into eqn. (1) yields an expression for the reaction rate in the presence of sodium perchlorate, eqn. (2).

$$v = k[HO^-]\,\frac{[CV]_{total}}{1+K[ClO_4^-]} \tag{2}$$

Therefore, the observed rate constant can be expressed in terms of the $NaClO_4$ concentration in the reaction medium,

$$k_0 = k[HO^-]\,\frac{1}{1+K[ClO_4^-]} \tag{3}$$

which can be readily linearized.

However, because the formation of the ion-pair is accompanied by the effect of the ionic strength due to the presence of substantial amounts of sodium perchlorate in the medium, the experimental data given in Table 2 cannot be directly processed by using eqn. (3) in a linearized form. Instead, the data were corrected by using NaCl inhibition data on the assumption that the inhibitory effect of the ionic strength introduced by both salts, in the absence of specific interactions, was similar.

Table 2 Corrected rate constant at $I = 0$ for the inhibition of the basic hydrolysis of CV obtained from eqn. (3).
$[CV] = 8.33 \times 10^{-6}$ M; [NaOH] = 0.15 M

$[ClO_4Na]$/M	$10^3\, k_0/s^{-1}$	$10^3\, k_{corr}/s^{-1}$
0	20.0	49.7
0.02	7.73	20.4
0.06	2.56	7.51
0.09	1.27	3.98
0.14	0.97	3.43

In this way, after establishing the range where the Brönsted–Bjerrum equation is fulfilled (where the Brönsted–Bjerrum equation is kept linear using the inert electrolyte NaCl), one can isolate the effects of the ion-pair formation and those arising from changes in the ionic strength of the medium.

After the pertinent corrected rate constant values are obtained, eqn. (3) in a linearized form can be used and the data found to conform to the proposed model. By fitting experimental data to this equation, the formation constant for the ion-pair was found to be 110 ± 14 $dm^3\ mol^{-1}$. Such a large constant is consistent with a strong association beween CV and sodium perchlorate.

Ascribing this experimental data to the formation of an ion-pair is consistent with the kinetic and spectroscopic evidence previously obtained for other carbonium ions such as tri-*p*-anisylmethylium,[8] tri-*p*-methoxyphenylmethylium[9] and triphenylmethylium.[10]

Financial support from the Dirección General de Investigación Científica y Técnica of Spain (Project PB93-0524) is gratefully acknowledged. J. C. M. thanks Xunta de Galicia for a Research Training Grant.

Received, 4th February 1997; Accepted, 14th May 1997
Paper E/7/00795G

References

1 G. N. Lewis, T. T. Magel and D. Lipkin, *J. Am. Chem. Soc.*, 1942, **64**, 1774.
2 H. H. Freedman, *Carbonium Ions*, ed. G. Olah and P. V. Schleyer, Interscience, New York, 1973, vol. IV.
3 C. D. Ridchie, *Can. J. Chem.*, 1986, **64**, 2239.
4 C. D. Ridchie, D. J. Wright, H. Der-Sing and A. A. Kamego, *J. Am. Chem. Soc.*, 1975, **97**, 1163.
5 E. F. G. Duynstee and E. Grunwald, *J. Am. Chem. Soc.*, 1959, **81**, 4540; E. F. G. Duynstee and E. Grunwald, *J. Am. Chem. Soc.*, 1959, **81**, 4542; M. J. Blandamer, B. Clark and J. Burgess, *J. Chem. Soc.*, *Faraday Trans. 1*, 1984, **80**, 1651; M. Valiente and E. Ródenas, *J. Phys. Chem.*, 1991, **95**, 3368; K. Tamura and N. Nii, *J. Phys. Chem.*, 1989, **93**, 4825; C. Izquierdo, J. Casado, A. Rodríguez and M. L. Moyá, *Int. J. Chem. Kinet.*, 1992, **24**, 19; C. A. Bunton and E. L. Dorwin, *J. Org. Chem.*, 1986, **51**, 4093.
6 J. R. Leis, J. C. Mejuto and M. E. Peña, *Langmuir*, 1993, **9**, 889.
7 P. Hervés and J. R. Leis, *J. Chem. Soc.*, *Perkin Trans. 2*, 1995, 2035.
8 C. A. Bunton and S. K. Huang, *J. Am. Chem. Soc.*, 1972, **94**, 3536.
9 M. J. Posble and P. A. H. Wyatt, *J. Chem. Soc.*, *Perkin Trans. 2*, 1972, 474.
10 J. N. Ride and P. A. H. Wyatt, *J. Chem. Soc.*, *Perkin Trans. 2*, 1973, 746; Y. K. Mo, R. E. Linder, G. Barth, E. Bunnenberg and C. Djerassi, *J. Am. Chem. Soc.*, 1974, **96**, 3309.