

Implications of a novel interpretation of the isosbestic point

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In an earlier article we articulated the isosbestic point from an entirely novel perspective,¹ (i.e., from the stand point of the steady state principle). Here we would like to report a new finding in the solvolysis⁵ reaction that the isosbestic point is invariant, contrary to the conventional belief that there is one degree of freedom.⁶ Furthermore, we find that many of the conventional descriptions of isosbestic point in the literature and allied websites appear to need reconsideration or revision.

Introduction

The existence of isosbestic point(s) in UV-visible spectra is demonstrated with the solvolysis of dichloromethylbenzene.^{2,5} From the time dependent spectra of solvolysis of dichloromethylbenzene (Fig. 1) two distinctly visible isosbestic points are observed.

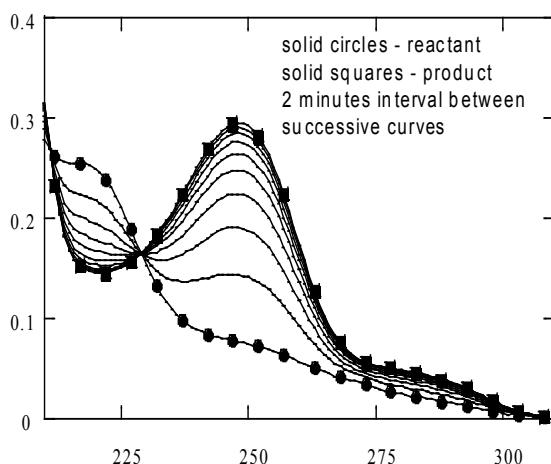


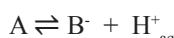
Fig. 1. Time-dependent UV-VIS spectrum of dichloromethylbenzene in water at 25°C.

In our recent new interpretation¹ we explained the reason for the appearance of isosbestic point at 233 nm from the stand-point of steady state approximation. In the following discussion, we address the implications of our new interpretation.

Discussion

The term ‘isosbestic point’⁷ is usually employed with reference to a set of absorption spectra, plotted on the same chart for a set of solutions in which the sum of the concentrations of two principal absorbing components, A and B, is constant. The curves of absorbance against wavelength for such a set of mixtures often all intersect at one or more points, called isosbestic points. Isosbestic points commonly appear when electronic spectra are determined on (a) a solution in which a chemical reaction is in progress (in which case the two absorbing components concerned are reactant and product); or (b) on a solution in which the

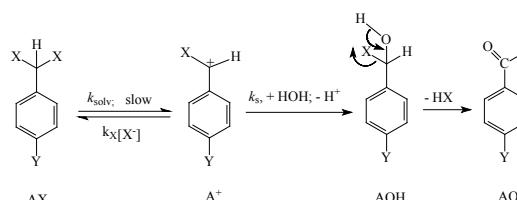
two absorbing components are in equilibrium and their relative proportions are controlled by the concentration of some other component, typically the concentration of hydrogen ions, e.g., in acid base indicator equilibrium.



The effect may also appear (c) in the spectra of a set of solutions of two unrelated non-interacting components having the same total concentration. If absorption spectra of the types considered in the foregoing three cases intersect not at one or more isosbestic points but over progressively changing wavelength, this is *prima facie* evidence in case (a) for the formation of a reaction intermediate in substantial concentration A→C→B.

Our findings (Fig. 1 and the corresponding Scheme 1) report two distinctly visible isosbestic points for the solvolysis of 1,1-dichlorotoluene/dichloromethylbenzene with α -chlorobenzyl carbocation as intermediate.

Scheme I



where X = Cl or Br or N_3

This does not conform with information available in the 1997 edition of the IUPAC Compendium of Chemical Terminology⁷ (in the absorption spectra in question, intermediate α -chlorobenzyl carbocation is observed in spite of the absence of intersection of spectra at progressively changing of wavelengths).

Furthermore, from a physical chemistry point of view,⁸ the isosbestic point has been defined as: during a chemical reaction, a point occurs in the absorption spectrum (i.e., a wavelength) where at least two chemical species (for example, reactant and product) have identical molar absorption coefficients, which remain constant as the reaction proceeds. A stable isosbestic point is evidence that a reaction is proceeding without forming an intermediate or multiple products. Against the backdrop of our findings (Fig. 1 and Scheme 1) of two isosbestic points in the solvolysis reaction and with the unequivocal evidence of presence of α -chlorobenzyl carbocation,^{2,5} again this description of the isosbestic point appears to need revision.

In addition, it has been reported⁹ that when a one-to-one (one mole of reactant yielding one mole of product)

chemical reaction (including equilibrium) involves a pair of substances with an isosbestic point, the absorbance of the reaction mixture at this wavelength remains invariant, regardless of the extent of reaction (or position of the equilibrium). This occurs because the two substances absorb light of that specific wavelength to the same extent, and the analytical concentration remains constant (at isosbestic point both molar absorptivities are the same). The isosbestic is defined¹⁰ as the wavelength, wave number or frequency at which the total absorbance of a sample does not change during a chemical reaction or physical change of the sample. A simple example occurs when one molecular entity is converted into another that has the same molar absorption coefficient at a given wavelength. As long as the sum of the concentrations of the two molecular entities is held constant there will be no change in the absorbance at this wavelength as the ratio of the concentration of the two entities is varied. The essence of these two descriptions^{9,10} is that the concentrations of the two substances remain constant at the isosbestic point, and their molar absorption coefficients are same. Again, against the backdrop of the interpretation of isosbestic point in our earlier publication,¹ even these descriptions need to be reconsidered. According to the interpretation¹ from the stand-point of steady state approximation, the concentration of the intermediate α -chlorobenzyl carbocation (Scheme 1) is constant; and as a consequence of this intermediate remaining constant, the absorbance (at 233 nm) is invariant (and not because the concentration of the two molecular species is constant). Thus, the popular blanket assertion that at the isosbestic point the concentration of the two molecular species remains constant, again, has to be redefined, at least for the solvolysis reactions described in Scheme 1.

Pouest *et al.*⁶ summarized the general conditions for the occurrence of the isosbestic point. Even though there is no general agreement on the conditions required, two major trends can be found concerning the number of absorbing components in the system:

- 1) A specific case was studied for a maximum of six absorbing species,¹¹ then simplified for an even more specific case of a complexation reaction with a maximum of four absorbing species.¹² These cases gave special conditions between products of molar absorptivities and stoichiometric coefficients.
- 2) More general cases without any limitation on the number of components were also studied. One study gave the most complete conditions on the system,¹³ stating that an isosbestic point can be shown when:
 - (a) the system is closed or results need to be corrected to correspond to a fixed overall concentration;
 - (b) the spectra of the limiting states of the system (e.g., before and after reaction) intersect; or
 - (c) the changes in the concentrations of the various components are linearly related, i.e., there is only one degree of freedom (e.g., the extent of reaction).

Returning to our system shown in Scheme 1 and the time-dependent spectra Fig. 1, in which we have interpreted the

isosbestic point on the basis of presence of the intermediate α -chlorobenzyl carbocation,¹ we can now calculate the number of components using the phase rule,¹⁴ viz., $F = C - P + 2$, where F is the number of degrees of freedom, C is the number of components and P is the number of phases. However, since our system is closed, the '2' (which represent the temperature and pressure variables) can be neglected; thus, the expression reduces to $F = C - P$. If this simplified phase rule is applied to our system at the isosbestic point, the number of components is 1 (intermediate α -chlorobenzyl carbocation); the number of phases is 1; and, as a result, the number of degrees of freedom is 0. Thus, in our system the isosbestic point is an invariant system (analogous to the triple point of water). In the conventional description of isosbestic point wherein we have two components and one phase, the number of degrees of freedom is 1. We infer that Pouest *et al.*'s conclusion that the number of degrees of freedom at the isosbestic point is one appears to be wrong, at least for our solvolysis reaction system.

Furthermore, Pouest *et al.*⁶ have concluded that when a reaction is followed by spectrophotometer, the appearance of one component is usually linked to the disappearance of one intermediate component, which can be highlighted by the fact that at some point during the reaction, the spectra no longer participates in the isosbestic point. A useful application of such a phenomenon could be the detection of the occurrence of an unknown or unusual component in an analyzed effluent for the process control or environmental purposes. Thus the use of the isosbestic point can be utilized for water quality monitoring. However, this application would again be erroneous with respect to our spectra (Fig. 1), as there is no observation of spectra which no longer participates in the isosbestic point.

According to Powles and Williams¹⁵ an isosbestic point may be found when some quantity is conserved in spite of the variation of other physical parameters. In our system (UV-spectroscopy) the absorbance is conserved in agreement with the observations of Powles and Williams. But again, with the backdrop of our new interpretation of isosbestic point the concentration of intermediate α -chlorobenzyl carbocation is also conserved with respect to time, i.e., there are two quantities which are conserved: absorbance and concentration of the intermediate α -chlorobenzyl carbocation.

An extremely important point with regard to interpretation of isosbestic points in this system (solvolysis of dichloromethylbenzene) is that at 233 nm the conventional definition of isosbestic point¹⁰ and our alternative interpretation¹ are applicable. However, when it comes to isosbestic point at 212 nm, the conventional interpretation of isosbestic point⁴ fails miserably. It can be easily perceived from the UV-spectrum of benzaldehyde that benzaldehyde would possibly not absorb at 212 nm and as a consequence there is no probability of its existence at this isosbestic point, i.e., 212 nm. According to the conventional definition, both dichloromethylbenzene and benzaldehyde should be present in constant ratio with their molar extinction coefficients identical. Since there is no

likelihood of existence of benzaldehyde at the isosbestic point of 212 nm, the conventional definition fails to explain the isosbestic point. At this stage of the development of interpretation of isosbestic point, our own interpretation¹ also fails to explain the presence of isosbestic point. In fact, this is unexplored territory: the challenge remains in front of us.

Acknowledgement

Rachuru Sanjeev would like to dedicate this manuscript to his late mother, Rachuru Vijaya, a conscientious teacher who saw to it that “the nature and nurture” that he received groomed him into a teacher with the same kind of quality.

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