

Quantitative Evaluation of Dissociation Mechanisms in Methylorange and Methylred

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Abstract—Several computational chemistry programs were evaluated as aids to teaching a part of qualitative analytical chemistry. Computational chemical calculations can predict absorption spectra, thus enabling the modeling of indicator dissociation mechanisms using a personal computer. An updated MNDO program among 51 programs was previously found to be the best predictor to explain the dissociation mechanisms of isobenzofuranones and sulfonephthaleins. Therefore, the further quantitative analysis was performed for methyl-orange and methyl-red. Computational chemical analysis can be used for quantitative explanation of indicator dissociation mechanisms.

Keywords—Computational chemistry, Dissociation, methylorange, methylred, Spectra.

I. INTRODUCTION

How quantitatively teach qualitative analytical chemistry is a challenged subject as an analytical chemist. Previously, a method to teach molecular interaction mechanisms in chromatography was quantitatively achieved using molecular mechanics and MOPAC programs. Furthermore, the reaction mechanisms of highly sensitive detections were also quantitatively described [1]. Farther study was carried out for simple detection, indicator's color changes by using updated computational chemical programs.

Color indicators have been the backbone of simple pH tests and titration analyses. The spectrophotometric determination of hydrogen ion concentrations by using color indicators was described [2]. The precision of indicator dissociation constants was evaluated and the dissociation mechanisms were described in detail. The pKa values were found to vary according to salt, temperature, and the laboratories where the work was conducted [3, 4]. The effects of salts and proteins on the spectra of some dyes and

indicators were studied [5]. The dissociation processes were described in detail by Kolthoff [3]. However, the absorption wavelength and electron density changes were not well described. The experimentally measured dissociation of phenolphthalein is described using four dissociation structures, where the ionization of two phenolic hydroxyl groups converts the neutral molecular form into the red quinoid form. Further dissociation from the quinoid structure to the alcoholic form eliminates the color. The dissociation mechanisms can also be described using three structures without the need for a transition structure [6].

The dissociation mechanisms, maximum wavelengths, and electron density maps of isobenzofuranones and sulfonephthaleins were, therefore, evaluated by *in silico* analysis despite the anticipated poor precision [7]. Further study was carried out for other popular indicators methyl-orange and methyl-red.

II. EXPERIMENTAL

The computer used was a PC model Prime INWIN BL672-4 with Intel Core i7 from Dospara, Yokohama, Japan. CAChe® programs were from Fujitsu (Tokyo, Japan). Indicators used are methyl-orange and methyl-red. The CAChe program provides different programs to calculate UV-visible spectra, including MNDO, PM5, INDO/S, and ZINDO. These programs were selected based on previous experiment [7]. The dissociation spectra of methylorange and methylred structures were calculated using these programs and used to evaluate the accuracy of the programs.

III. RESULTS AND DISCUSSION

The basic structures of methyl-orange and methyl-red molecules drawn and optimized using MM2 program are shown in Figures 1, respectively.

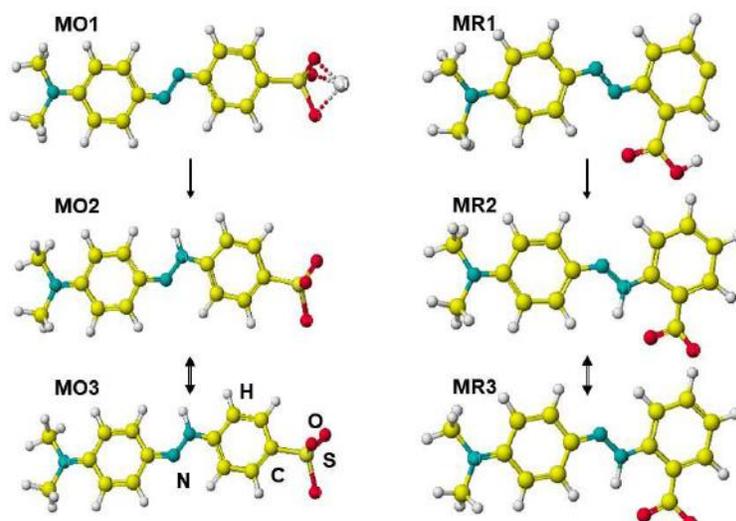


Figure 1. Dissociation structures of methyl-orange (MO) and methyl-red (MR)

There are many computational chemistry programs available to create electronic spectra; however, the previous study concluded MNDO program demonstrated the best predicted spectra. Therefore, the resonance structures of methylorange and methylred shown in Figure 2 were calculated using MNDO programs. These resonance structures were combinations of methyl-orange 2 and methyl-orange 3 (MO2+MO3) in Figure 1, and methyl-red 2 and methyl-red 3 (MR2+MR3) in Figure 1, respectively. The resonance structures of methylorange and methylred were further optimized using MM2+ZINDO and PM5+ZINDO for their comparison. Previous analysis demonstrated that MM3 was

found to show weak absorption spectra and did not provide definite information about the maximum absorption wavelengths. Structures optimized using MM3 exhibited weak molar absorptivities and red shift, and semi-empirical and semi-empirical combinations did not work in many cases, with computer error messages being generated. Therefore, MM2 was chosen as the initial program, and the spectra of resonance structures of methyl-orange and methyl-red were calculated using CAChe programs. The results are summarized in Table 1, where some absorption wavelengths are given following in their absorption strength.

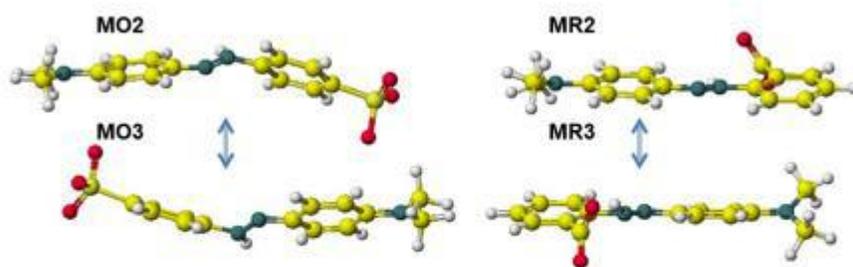


Figure 2. Conformation of resonance structures of methyl-orange (MO2=MO3) and methyl-red (MR2=MR3), Atoms: see Figure 1.

The evolution of computational chemistry programs should improve the precision of predicted spectra. However, ZINDO gave a relatively better wavelength prediction. A Zerner modification is seemed to improve the original INDO performance for methyl-orange and methyl-red as that for

phenolphthalein. The optimized spectra using PM5 demonstrated the lower maximum absorption wavelength as demonstrated for phenolphthalein. The optimized structures of MR2 and MR3 demonstrated intra-hydrogen bonding between amino-hydrogen and carboxyl-oxygen, and

demonstrated the higher maximum absorption wavelength. The atomic distance between hydrogen and nitrogen was a little longer (2.33Å), and that between hydrogen and oxygen was a little shorter (0.95 Å). In aqueous solution, intra-molecular hydrogen bonding should not be formed; therefore, cut the bond between hydrogen and oxygen, then optimized these spectra using ZINDO. The adjusted spectra showed the relatively closed to measured their maximum absorption

wavelength. The results are summarized in Table 1. The predicted spectra are shown in Figure 3.

The small wavelength difference cannot be justified because the solvent effect was not included in the calculation. Elimination of intra-molecular hydrogen bonding simplified these spectra in visible region. Originally three absorption maximum were observed, but their sub-absorptions were disappeared and concentrated into their lowest absorption wavelength.

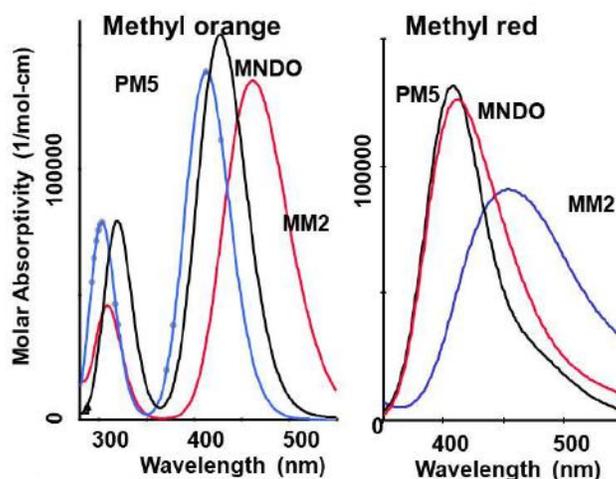


Figure 3. Predicted spectra of methyl-orange and methyl-red, Abbreviation of PM5, MNDO, MM2: see in text.

The comparison of calculated spectra indicates that a selection of program set was not easy for a variety of compounds. This is a tedious process to find the best program set to obtain an identical spectrum with the measured spectrum. However, we have to recognize the

estimated spectra were calculated *in vacua*, but the experimental spectra were measured in pH controlled aqueous solution, This means that computational chemically estimated spectra should be used as the relative information to study the color indicator mechanisms.

Table 1 Properties of indicators

Program	MNDO-ZINDO		PM5-ZINDO		MM2-ZINDO	
	MWL	MA	MWL	MA	MWL	MA
MO1	278.9	39712	336.1	81005	420.7	108086
MO2	334.7	86000	334.9	80140	401.3	106360
MO3	539.9	70120	522.7	83300	535.4	92125
MO2+MO3	427.3	163600	412.4	139240	461.5	136585
MR1*	299.2	62170	321.5	68140	417.2	2078
MR2*	303.1	64754	334.8	70400	394.1	93682
MR2	403.8	42224	445.5	67240	-	-
MR3*	302.5	65596	337.7	71810	495.7	95068
MR3	407.1	41937	450.7	68910	-	-
MR2+MR3#	352.5>421.9>504.4		325.4>247>249		453.1>362.4>522.2	
MR2+MR3	407.3	123820	407.7	131795	455.5	61116

MF: molecular structure; MO1-3: methyl orange 1-3 in Figure 1. MR1-3: methyl red 1-3 in Figure 2; MO2+MO3 and MR2+MR3: resonance forms in Figure 3; MWL: maximum wave-length (nm); MA: molecular absorptivity (1/mol-cm); *: original conformation with irregular bonding; #: original maximum multi wave-length (nm) followed the intensity.

IV. CONCLUSION

Computational chemical analysis can help to teach qualitative analytical chemistry better. For spectra predictions and the visualization of the electron-transfer mechanisms for color indicators, combinations of MNDO with CI seemed to give the best results for the resonance structures of methyl-orange and methyl-red. Improvements in these programs will further improve the teaching of analytical chemistry. The estimation of solvent effects remains a challenge.

Abbreviations of computational chemical programs

Following programs are listed in CAChe programs, however, the selection guide is not available. First, constructed structures were optimized by MM2; then their spectra were calculated using a semi-empirical program available. First, constructed structures were optimized by MM2; then their spectra were calculated using a semi-empirical program

CI: Configuration Interaction [8, 9]

INDO/S: INDO for spectroscopy [10, 11]

MNDO/d: MINDO modified NDDO with d-orbital [12]

PM5: Parametric Model 5; Version-up program of PM3 [13]

ZINDO: reference [8]

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