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Ultraviolet Spectra of Acetic Acid, Glycine, and Glyphosate

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Abstract

The influence of pH on the ultraviolet spectra of 0.001, 0.005, and 0.010 M glyphosate, glycine, and acetic acid was investigated. Each dilution of each acid was adjusted to acidic, neutral, and basic pH values. Ultraviolet spectra were recorded from 300 to 200 nm for each acid-dilution-pH combination. The wavelength of maximum absorption (λ_{max}) of glyphosate and glycine was slightly higher in the high pH solutions than in the neutral and low pH solutions. The λ_{max} of acetic acid was apparently unaffected by changes in pH. Molar extinction coefficients (ϵ) at λ_{max} increased with pH for all three acids. Regression analysis of the absorbance versus concentration for each acid-pH combination indicated linear relationships. Coefficients of determination (r^2) were greater than 0.88 at both 210 and 215 nm for all acids and pH values.

Introduction

Ultraviolet (UV) spectroscopy of organic compounds usually indicates little about structural characteristics. Organic compounds that contain certain functional groups such as carboxyls, carboxylates, aldehydes, ketones, and esters have UV absorption maxima in the range of 190 to 210 nm. UV spectra of these moieties are not as diagnostic as infrared spectra, but may be used in quantifying the chromophore bearing species (Willard, et al., 1974). The mechanism of UV radiation absorption of these single chromophores is the excitation of p-orbital non-bonding electrons to antibonding σ -orbitals as well as $\pi \rightarrow \pi^*$ of the carboxylate carbon. The transitions are $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, and occur on the carbon-oxygen unsaturated bonds (Parikh, 1974; Scott, 1964).

Glyphosate, or N-phosphonomethyl glycine, (Fig. 1), is an organic acid and the active ingredient in the herbicide Roundup[®] marketed by the Monsanto Chemical Corporation. The rapid adsorption of glyphosate by soils and soil compounds has made the compound the focus of many studies (Hance, 1976; Sprankel et al., 1975; Torstensson and Amisep, 1977). Generally, these studies have shown glyphosate to be strongly adsorbed by soils and soil constituents under a variety of conditions. Certain studies have been conducted to examine the UV spectra of solution-phase, glyphosate-metal complexes and have failed to show the contribution of the uncomplexed carboxyl and carboxylate groups of glyphosate (Glass, 1984; Glass, 1987; McBride and Kung, 1989). The UV absorption of the acid functionality has been used in

the analytical determination of glyphosate thereby demonstrating its importance (Burns, 1983; McConnell and Hossner, 1985; Errata, 1991).

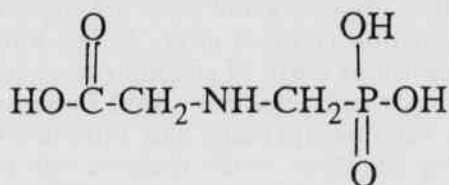


Fig. 1. Glyphosate

The objective of this research was to examine the UV spectra of glyphosate and two other carboxylic acids, and determine the wavelength of maximum absorbance (λ_{max}) and the molar extinction coefficients (ϵ) at λ_{max} , 215 nm, and 210 nm as influenced by pH. Further, regression analysis was used to determine the linearity of graphs of UV absorbance at 210 and 215 nm versus acid concentration.

Materials and Methods

Organic Acids.—Glyphosate (99%) was obtained from the Monsanto Chemical Corporation and used without further purification. Reagent grade glycine and acetic acid were purchased from Fischer Scientific Supply of Plano, Texas and also used without further purification. Dilutions of acetic acid were quantified with titrametric

techniques with standard base. Samples of the acids were then diluted to 0.010, 0.005, and 0.001 M. Each sample was adjusted to pH values near 3, 7, and 10 with NaOH.

Instrumentation.—The ultraviolet spectra of the protonated and deprotonated acids at the three concentrations were recorded from 300 to 200 nm on a Perkin-Elmer Model 25 UV-visible spectrophotometer. Matched silica-quartz cuvettes with a 1.0 cm path length from Perkin-Elmer (Lot Number 14993) were used to contain the diluted acids. Scan speed was set at 20 nm/min. and 1.0 nm/in. The spectra of the 0.010 M solutions were used to determine the λ_{\max} , the absorbance maxima, and the ϵ at λ_{\max} .

The absorbances and ϵ of the samples were also recorded at 210 and 215 nm, and analyzed using linear regression. Regression analysis gave estimates of slopes and intercepts, and the linearity of the relationship between absorbance and concentration for each acid and pH.

Results and Discussion

Spectra of all three compounds at the three concentrations and pH values indicate UV absorbance from approximately 220 to below 200 nm. This is the approximate wavelength range organic acids are expected to absorb UV radiation (Willard et al., 1974). The total absorbance spectra of 0.010 M solutions of glyphosate increased with pH and exhibited a shift in absorption maxima from <200 nm (pH 2.83 and 7.01) to 214 nm (pH 10.01) (Fig. 2). These results disagree with reports that state glyphosate is UV transparent (Glass, 1984; Glass, 1987).

The λ_{\max} for the low and neutral pH solutions of 0.010 M glyphosate and glycine was found to be near or below 200 nm. As the pH was increased, the λ_{\max} of glyphosate and glycine increased to 214 and 210 nm, respectively. The acetic acid solutions exhibited λ_{\max} at 204, 200 and 204 nm for the low, neutral and high pH solutions, respectively (Table 1). The trend of increasing pH and increasing λ_{\max} that was evident in the spectra of glyphosate and glycine was not observed with acetic acid because of its monoprotic structure. Amino acids and diacids differ from monoprotic acids in that they generally show an increase in absorbance and a shift to longer wavelengths (bathochromic shift) with increasing pH (Greenstein and Winitz, 1961; Parikh, 1974). The increase in absorbance and the bathochromic shift are attributed to the auxochrome created by dianionic structures. The λ_{\max} of monoprotic acetic acid remained relatively constant with increasing pH due to absence of any auxochromes.

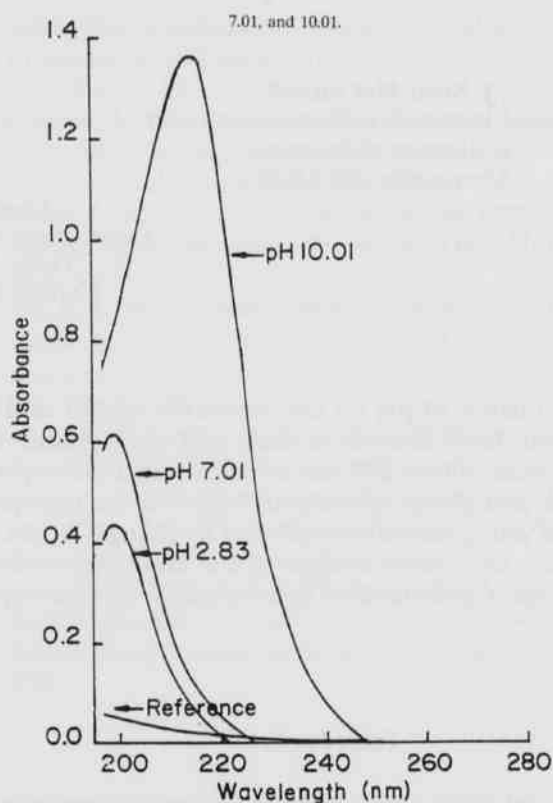


Fig. 2. Absorbance spectra of 0.010 M glyphosate solutions adjusted to pH 2.83, 7.01, and 10.01.

Table 1. Wavelength of maximum absorption (λ_{\max}), maximum absorbance (A_{\max}), and molar extinction coefficient (ϵ_{\max}) of ultraviolet spectra of 0.010 M solutions of glyphosate, glycine, and acetic acid at low, neutral, and high pH values.

	Glyphosate			Glycine pH			Acetic Acid		
	2.83	7.01	10.01	3.03	6.99	9.97	3.49	6.94	10.13
λ_{\max}	<200	<200	214	<200	201	210	204	200	204
A_{\max}	0.430	0.615	1.37	0.510	0.650	1.16	0.325	0.670	0.885
ϵ_{\max}	43	62	137	51	65	116	33	67	89

The ϵ at the λ_{\max} (ϵ_{\max}) for all three acids was found to range between 33 and 137, and increase with increasing pH (Table 1). Three groups of similar ϵ_{\max} are apparent, and related to the solution pH. The low pH solutions of glyphosate, glycine and acetic acid had similar ϵ_{\max} that

ranged from 33 to 51. All three ϵ_{\max} were found to increase slightly, ranging from 62 to 67, as the pH was raised from acid to neutral. Increasing the pH of the solutions to near 10 resulted in large increases in ϵ_{\max} with increasing pH, up to 89, was found with the acetic acid solutions. The large increases in the ϵ_{\max} values of the glyphosate and glycine solutions indicate that the additional lone pairs of electrons present in the phosphamide of glyphosate and the amino group of glycine act as an auxochrome causing both a bathochromic shift and an increase in absorbance. The degree of protonation of these auxochrome groups generally affects the availability of the lone pairs of electrons for $n \rightarrow \pi^*$ transitions (Parikuh, 1974). These experimental results demonstrate that the degree of protonation is a major determinant of the UV absorption characteristics of glyphosate, glycine and acetic acid.

Regression analysis of the concentrations of the individual acids and their UV absorptions indicated a high degree of linearity at 210 and 215 nm for the three pH values tested (Fig. 3). The r^2 exceeded 0.9 in all regression lines at 215 nm, and in all but one at 210 nm. The high degree of linearity indicates that these wavelengths may be used for analytical determinations of glyphosate, glycine, or acetic acid in aqueous solutions. The presence of other carboxylic acids or mixtures of these three would probably interfere in this type analysis unless a suitable separations technique were employed.

The mean of the slopes of the regression lines (215 nm) for low and neutral pH solutions of glyphosate and glycine, and all three acetic acid solutions was 18.20 with a standard deviation of ± 3.07 . The range of the slopes for these solutions was from 13.59 to 23.39, thereby indicating little difference in the slopes of these regression lines. Solutions of high pH glycine and glyphosate had much higher slopes than their lower pH analogs or the acetic acid solutions. This corresponds with the increases in ϵ_{\max} and changes in λ_{\max} observed in the UV spectra of the high pH glyphosate and glycine solutions. The increased absorbance of the high pH glycine and glyphosate solutions increased the slope of the regression line.

Conclusions

Solutions of glyphosate, glycine, and acetic acid were shown to absorb ultraviolet radiation from 220 to 200 nm. Wavelength of maximum absorption and ϵ_{\max} for glyphosate and glycine were similar at low and neutral pH. Increased pH resulted in increased λ_{\max} and ϵ_{\max} . The λ_{\max} of the acetic acid solutions was seemingly unaffected by pH, while the ϵ_{\max} was less affected by pH than the other acids.

Regression analysis of the concentrations of the acids and their UV absorptions indicates a linear relationship

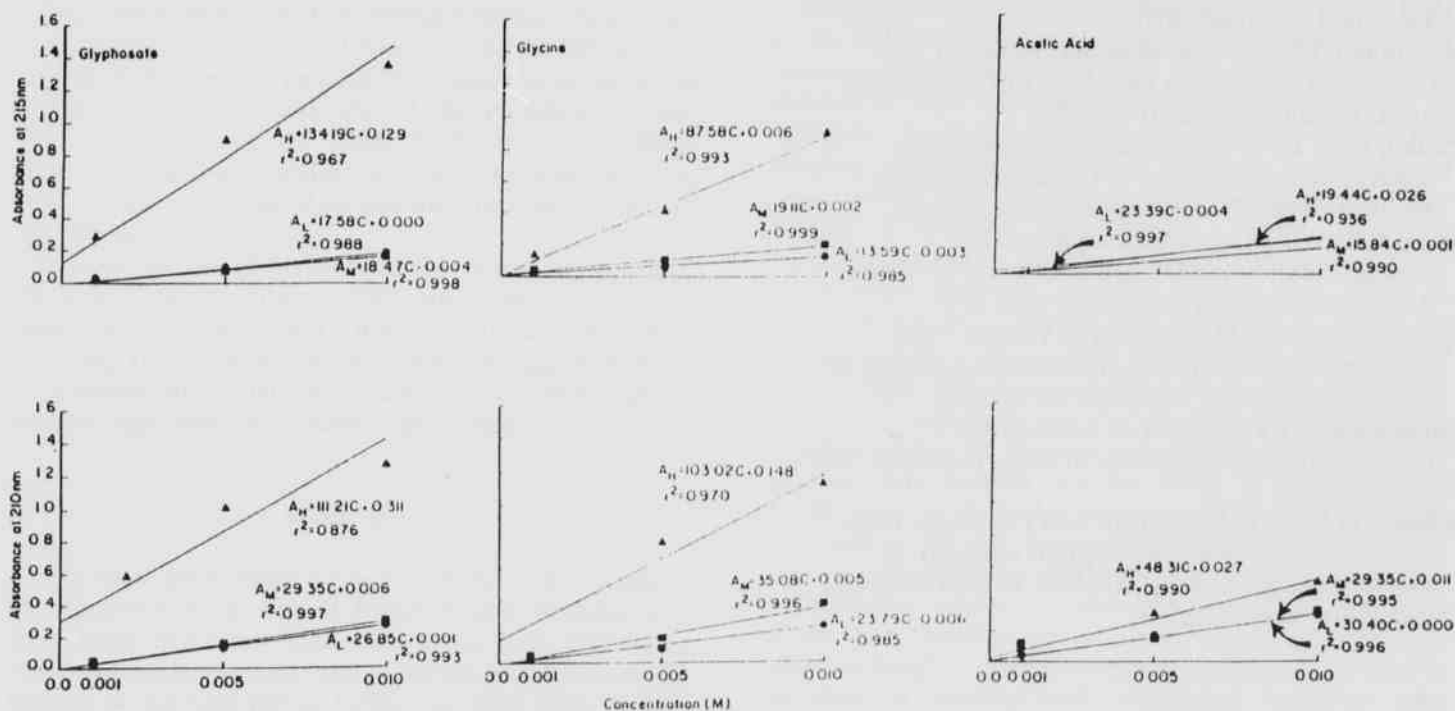


Fig. 3. Slope, intercept, and coefficient of determination (r^2) of absorbance versus concentration of glyphosate, glycine, and acetic acid at high pH (A_H), moderate pH (A_M), and low pH (A_L) values.

at 210 and 215 nm. The slopes of the regression lines were found to be similar for low and neutral pH solutions of glyphosate and glycine, and for all acetic acid solutions. Much higher slopes were found for high pH solutions of glyphosate and glycine. The linear relationship between concentration and UV absorbance of glyphosate provides a useful analytical method for the determination of glyphosate, and similar acids, in aqueous solutions.

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