on both monocots and dicots in the same vermiculite culture but using subirrigation in a woodbox.

Testing of the soil-applied activity of various iodides was undertaken using routine greenhouse procedures. The chemical was mixed thoroughly in the top 7 cm of soil in pots. Seeds were planted in pots about 2 cm below the surface of the soil composed of 0.5 silt top soil, 0.25 sand, and 0.25 peat, and fertilized with urea, 11-55-0, and potash in a rate of 60, 20, and 60 kg/ha for N, P_2O_5, and K_2O, respectively. Herbicidal dosages are expressed in terms of kg/ha. The treatments were evaluated 4 weeks after seeding and were at least duplicated.

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Shi-chow Chen*
Richard M. Elofson

Special Projects Division
Alberta Research Council
Edmonton, Alberta T6G 2C2, Canada

Spectrophotometric Determination of Dissociation Constants of Selected Acidic Herbicides

pK_a values have been determined for ten acidic herbicides and one fungicide using a spectrophotometric method. pK_a values are reported for [(4-chloro-o-tolyl)oxy]acetic acid (MCPA), 3.13; (±)2-[(4-chloro-o-tolyl)oxy]propionic acid (mecoprop), 3.11; (2,4-dichlorophenoxy)acetic acid (2,4-D), 2.87; 2-(2,4-dichlorophenoxy)propionic acid (dichlorprop), 2.86; (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T), 2.85; 2-(2,4,5-trichlorophenoxy)propionic acid (fenoprop), 2.83; 3,6-dichloro-o-anisic acid (dicamba), 1.90; 2-sec-butyl-4,6-dinitrophenol (dinoseb), 4.62; 4,6-dinitro-o-cresol (DNOC), 4.46; 3,5-dibromo-4-hydroxybenzonitrile (bromoxynil), 4.20; and pentachlorophenol (PCP), 4.71. The pK_a values for (o-chlorophenoxy)acetic acid (2-CPA), 3.00, and (p-chlorophenoxy)acetic acid (4-CPA), 3.05, have been included for comparative purposes. The pK_a values for 2-CPA, 4-CPA, MCPA, 2,4-D, and 2,4,5-T from this study were in close agreement with those previously reported from potentiometric and conductimetric determinations. The pK_a values for 4-[(4-chloro-o-tolyl)oxy]butyric acid (MCPB), 4-(2,4-dichlorophenoxy)butyric acid (2,4-DB), 4-amino-3,5,6-trichloropicolinic acid (picloram), 3,6-dichloropicolinic acid (M-3723), and 2,3,5-triiodobenzoic acid (TIBA) could not be determined using the spectrophotometric method.

The degree of dissociation of weakly acidic organic herbicides determines not only their entry into plants, both via leaf surfaces (Simon and Beevers, 1952) and roots (Grover, 1968), but also their adsorption, mobility, and deactivation in soil (Adams, 1973) and water (Weber, 1972). Thus, in order to gain an understanding of the fate and behavior of these biologically active compounds in the environment, accurate ionization constants or pK_a values (negative logarithm of the ionization constant) for these herbicides are necessary.

pK_a values for several of these herbicides (MCPB, 2,4-DB, mecoprop, dichlorprop, fenoprop, bromoxynil, dinoseb, dicamba, picloram) have been published in reviews (Bailey and White, 1965; Weber, 1972) with no reference to the methodology employed in their determination. However, even when the methodology has been described, there is wide disagreement in the pK_a values for many of these weakly acidic herbicides (MCPA, 2,4-D, 2,4,5-T, picloram). For example, the reported pK_a values for 2,4-D varied from 2.64–3.28 (Audus, 1949; van Overbeek et al., 1951; Ketelaar and Gersmann, 1952; Wedding et al., 1954; Matell and Lindenfors, 1957; Wershaw et al., 1967;

and Nelson and Faust, 1969).

Although most herbicide pK_a determinations have been made using either the potentiometric titration or conductimetric methods, the spectrophotometric method has been used (Weber, 1967) to determine the pK_a values for several triazine herbicides. One of the main advantages of the spectrophotometric method is that pK_a determinations can be made at solute concentrations in the range 10^{-3} to 10^{-5} M, whereas, accurate pK_a values cannot be achieved using the potentiometric titration method unless the pK_a value is greater than the negative logarithm of the molar concentration. Consequently, the potentiometric titration method is not ideal for many herbicides because of their low solubilities. The conductimetric method, although suitable at low concentrations, has to be carried out at a number of dilutions, with each conductimetric value requiring different activity corrections. The practical work is time-consuming, and the activity correction calculations are quite tedious in contrast to those required by the spectrophotometric method. All three methods have been recently described in detail by Albert and Serjeant (1971).

Table I. pK_a Values of Acidic Herbicides

Structural Formula	Common name	Chemical name	Stock soln, M	Analytical wave length	pK_a values
(o-chlorophenoxyacetic acid structure)	2-CPA	(o-Chlorophenoxy)acetic acid[c]	0.010[gj]	273	2.99 ± 0.02[m] 3.00 ± 0.05[m]
(p-chlorophenoxyacetic acid structure)	4-CPA	(p-Chlorophenoxy)acetic acid[c]	0.003[fj]	273	3.04 ± 0.06 3.05 ± 0.06
(MCPA structure)	MCPA	[(4-Chloro-o-tolyl)oxy]acetic acid[c]	0.005[fj]	230	3.13 ± 0.05 3.12 ± 0.06
(Mecoprop structure)	Mecoprop	(±)2-[(4-Chloro-o-tolyl)oxy]propionic acid[c]	0.005[fj]	230	3.11 ± 0.06 3.10 ± 0.05
(2,4-D structure)	2,4-D	(2,4-Dichlorophenoxy)acetic acid[c]	0.005[fk]	230	2.87 ± 0.06 2.86 ± 0.05
(Dichlorprop structure)	Dichlorprop	2-(2,4-Dichlorophenoxy)propionic acid[c]	0.005[gk]	230	2.86 ± 0.06 2.85 ± 0.06
(2,4,5-T structure)	2,4,5-T	(2,4,5-Trichlorophenoxy)acetic acid[c]	0.00167[hk]	296	2.85 ± 0.05[m] 2.84 ± 0.06[m]
(Fenoprop structure)	Fenoprop	2-(2,4,5-Trichlorophenoxy)propionic acid[c]	0.00167[hk]	294	2.84 ± 0.03[m] 2.82 ± 0.06[m]
(benzoic acid structure)		Benzoic acid[d]	0.001[gi]	230	4.17 ± 0.06[m] 4.17 ± 0.06[m]
(Dicamba structure)	Dicamba	3,6-Dichloro-o-anisic acid[a]	0.004[gl]	280	1.90 ± 0.05 1.89 ± 0.04
(Dinoseb structure)	Dinoseb	2-sec-Butyl-4,6-dinitrophenol[a]	0.00625[gi]	270	4.62 ± 0.01[m] 4.61 ± 0.02[m]
(DNOC structure)	DNOC	4,6-Dinitro-o-cresol[b]	0.005[ei]	270	4.46 ± 0.03[m] 4.46 ± 0.02[m]
(Bromoxynil structure)	Bromoxynil	3,5-Dibromo-4-hydroxybenzonitrile[a]	0.0025[ei]	283	4.21 ± 0.05 4.19 ± 0.05[m]
(Pentachlorophenol structure)	PCP	Pentachlorophenol[b]	0.0005[gi]	250	4.71 ± 0.05 4.70 ± 0.03

[a] Analytical grade compounds used without further purification. [b] Reagent grade compounds used without further purification. [c] Recrystallized from ethanol–water using decolorizing carbon. [d] Recrystallized from water using decolorizing carbon. [e] 1-mm cells. [f] 5-mm cells. [g] 10-mm cells. [h] 50-mm cells. [i] 0.01 N HCl. [j] 0.1 N HCl. [k] 0.2 N HCl. [l] 1.5 N HCl. [m] Determined using the Radiometer pH meter.

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Table II. Comparison of pK_a Values Obtained for Some Phenoxy Herbicides

Reference	Method	pK_a values				
		2-CPA	4-CPA	MCPA	2,4-D	2,4,5-T
Cessna and Grover (this study)	Spectrophotometric	3.00	3.05	3.13	2.87	2.85
Behaghel (1965)	Conductimetric	2.99	3.02			
Matell and Lindenfors (1957)	Conductimetric		3.01	3.11	2.90	2.83
Nelson and Faust (1969)	Potentiometric	2.98	2.99	3.09	2.77	2.89

This paper presents pK_a values for a number of acidic agrichemicals including herbicides which were determined using the spectrophotometric method. The herbicides studied included phenoxy acids, benzoic acids, phenols, and pyridine derivatives.

EXPERIMENTAL SECTION

Appartus. The following apparatus was used: Beckman Century SS pH meter equipped with a Fisher 0.25 in. × 5 in. microprobe combination electrode; Radiometer pH meter 4 equipped with a Beckman glass pH electrode and a Beckman calomel electrode; Perkin-Elmer Model 124 Coleman double-beam grating spectrophotometer synchronized with a Perkin-Elmer Model 56 recorder; quart cells: 1, 5, 10, 50 mm; Corning Model AG-2 water still.

pK_a Determinations. The concentrations of the buffer and stock solutions, the choice of an analytical wavelength, and the determination of the optical densities of the anionic and molecular forms of each compound were performed as described by Albert and Serjeant (1971). Buffer solutions over the pH ranges of 3.2 to 4.4 and 4.2 to 5.0 were prepared with formic acid and acetic acid, respectively. For pH values less than 3.2, HCl solutions were used. All pH and optical density measurements were made at room temperature on solutions of each compound prepared by adding 5.0 mL of stock solution (see Table I) to 45 mL of the appropriate buffer or HCl solution. The pK_a values and corresponding scatter were calculated as described by Albert and Serjeant (1971).

RESULTS AND DISCUSSION

Albert and Serjeant (1971) have suggested that reliable and reproducible pK_a values should have a maximum scatter of 0.06 unit. All of the pK_a values determined in this study (see Table I) fall within this range. Since the maximum concentration of the anionic species for any of the compounds studied was less than 10^{-3} M, the activity coefficient for the anion would be close to unity and its activity would be approximately equal to its concentration. Thus, the pK_a values calculated for the dilute hydrochloric acid solutions were thermodynamic pK_a values. Thermodynamic pK_a values were also obtained for the buffer solutions (0.01 M) by applying the Debye-Hückel activity correction for the ionic strength of the buffer solutions (Albert and Serjeant, 1971).

The pK_a value of 4.17 for benzoic acid compared very well with the accepted thermodynamic pK_a value of 4.18–4.20 (Albert and Serjeant, 1971) and served as a check on the accuracy of the instruments used. Little error in the observed pK_a values would have been introduced by the day to day variation in room temperature (22–26 °C) as the pK_a values of both carboxylic acids and phenols vary little over the temperature range of 20 to 25 °C (Albert and Serjeant, 1971). The results of the present study are in close agreement (see Table II) with the pK_a values determined potentiometrically at the lowest ionic strengths used by Nelson and Faust (1969) and with those determined conductimetrically by Behaghel (1926) and Matell

and Lindenfors (1957).

Substituents affect the acidic strengths of both carboxylic acids and phenols. Because of conjugation of the phenyl ring with the lone pair of electrons on the phenolic oxygen, both inductive (I) and mesomeric (M) effects of substituents on the phenyl ring determine the acidic strengths of phenol derivatives (phenol; $pK_a = 10.00$; Ko et al., 1964). The pK_a values found for dinoseb and DNOC (see Table I) were intermediate between those resulting from the acid strengthening nitro ($-I$, $-M$) groups (2,4-dinitrophenol; $pK_a = 4.09$; Robinson, 1967a) and the acid weakening 6-alkyl ($+I$, $+M$) group (*o*-cresol; $pK_a = 10.32$; Herington and Kynaston, 1957). The observation that dinoseb was a slightly weaker acid than DNOC may be due to greater steric inhibition to solvation of the phenoxide anion by the *sec*-butyl group. The observed pK_a value of 4.46 for DNOC was in very good agreement with that ($pK_a = 4.47$) determined spectrophotometrically by Robinson (1967a), whereas the observed pK_a value (4.62) for dinoseb differed from that (4.40) reported by Weber (1972). The *o*-bromo ($-I$, $+M$) substituents (2,6-dibromophenol; $pK_a = 6.69$; Robinson, 1967b) and *p*-cyano ($-I$, $-M$) group (*p*-cyanophenol; $pK_a = 7.97$; Fickling et al., 1959) of bromoxynil and the chloro ($-I$, $+M$) substituents (2,4,6-trichlorophenol; $pK_a = 6.23$; Fischer et al., 1967; 3,5-dichlorophenol; $pK_a = 8.18$; Robinson, 1964) of pentachlorophenol are acid strengthening. There was some difference between the observed pK_a value (4.20) for bromoxynil and that (4.08) reported by Weber (1972), whereas the observed pK_a value (4.71) for pentachlorophenol compared well with the spectrophotometrically determined value (4.74) of Drahonovsky et al. (1971).

Conjugation also occurs with benzoic acid derivatives (benzoic acid; $pK_a = 4.20$; Bowden and Shaw, 1971) between the phenyl ring and the carboxyl group. The acid strengthening effect of the chloro substituents of dicamba (2,5-dichlorobenzoic acid; $pK_a = 2.64$; Mather and Shorter, 1961) and the *o*-methoxy ($-I$, $+M$) group (*o*-methoxybenzoic acid; $pK_a = 4.09$; Srivastava, 1966) may be enhanced by the presence of substituents in both ortho positions. The steric pressure exerted by these groups may force the carboxyl group out of the plane of the ring resulting in an increase in acidic strength as the acid weakening $+M$ effect from the phenyl ring would be decreased. The observed pK_a value of 1.90 was in good agreement with that (1.93) reported by Weber (1972).

However, conjugation between the phenyl ring and the carboxyl group in the series of substituted phenoxyacetic and 2-(phenoxy)propionic acids is not possible; thus, only the inductive effects of the methyl and chloro substituents on the phenyl ring will affect the pK_a values of these compounds. 4-CPA was found to be a weaker acid than 2-CPA and this may reflect the greater separation between the *p*-chloro substituent and the carboxyl group. The addition of an *o*-methyl group (MCPA) further decreased the acidic strength of 4-CPA, whereas an *o*-chloro substituent (2,4-D) markedly increased its acidic strength. The addition of a third chloro substituent in the meta

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position (2,4,5-T) resulted in a further increase in acidic strength. Similar effects were observed with the 2-(phenoxy)propionic acid series.

It was not possible to determine the pK_a values of MCPB and 2,4-DB because the difference in the optical densities of the anionic and molecular forms for both compounds was negligible. Determination of the pK_a values for picloram and M-3723 also was not possible because the optical densities of the monoprotonated forms of these two pyridine derivatives could not be measured. The pK_a value for TIBA could not be determined because of its limited solubility in 3.0 N HCl solution.

ACKNOWLEDGMENT

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Allan J. Cessna*
Raj Grover

Herbicide Behavior in the Environment Section
Agriculture Canada
Research Station
Regina, Saskatchewan, Canada S4P 3A2

Urinary Metabolites of [¹⁴C]Photodieldrin in Male Rabbits

Oral and intraperitoneal treatment of male rabbits with [¹⁴C]photodieldrin resulted in the excretion of about 50% of the administered dose in urine. More than 98% of the radioactivity in urine was water soluble, about 30% of which was hydrolyzable with glucuronidase and about 6% with HCl. The remaining unhydrolyzable radioactivity was unextractable. Photodieldrin *trans*-diol was the major product followed by photodieldrin ketone and remaining minor unidentified products.

Photodieldrin, an environmental "terminal residue" of the commonly used insecticides aldrin and dieldrin (Rosen et al., 1966; Khan et al., 1974), is considerably persistent in the environment (Suzuki et al., 1974; Reddy and Khan 1975a). It is metabolized by some insects (Khan et al., 1969; Reddy and Khan, 1977) and mammals (Klein et al., 1969, 1970, 1973; Dailey et al., 1970, 1972; Reddy and Khan, 1974, 1975b) to lipophilic and hydrophilic metabolites. Oral and intraperitoneal treatment of male rabbits resulted in excretion of about 50% (55% when intraperitoneally and 48.5% when orally administered) of the administered dose in urine and only 3% in feces in 9 days (Reddy and Khan, 1975b). Less than 1% of the radioactivity in urine was extractable with ether, remaining being water soluble. These organosoluble metabolites included photodieldrin ketone, photodieldrin *trans*-diol, photodieldrin, and four other unidentified products (Reddy and Khan, 1975b). This report provides information about the nature of the water-soluble conjugated products of urine of male rabbits dosed with [¹⁴C]photodieldrin.

MATERIALS AND METHODS

Chemicals. [¹⁴C]Photodieldrin was prepared in this laboratory and was free of interferring chemicals as checked by thin-layer chromatography (TLC) and gas chromatography (GC) (Reddy and Khan, 1975b).

Animals. Male rabbits (Scientific Small Animals), 8 to 9 months old (about 3 kg body weight), were injected or fed about 30 μCi (30 mg/kg) of [¹⁴C]photodieldrin in corn oil (Reddy and Khan, 1975b). Urine and feces were collected separately for every 24 h for 9 days. A 0.1-mL aliquot of the urine was analyzed for total radioactivity by scintillation counting. About 50 mL of urine was extracted, three or four times, with 50 mL of ether. The pooled ether extract was evaporated to dryness and the residue redissolved in acetone and counted for organosoluble radioactivity. The acetone solutions of the urine extracts of 9 days were pooled, concentrated, and analyzed by TLC (Silica Gel F-254, 0.25 mm plates) using benzene–ethyl acetate (3:1). Plates were then exposed to x-ray film and autoradiographed (Reddy and Khan, 1975b,