

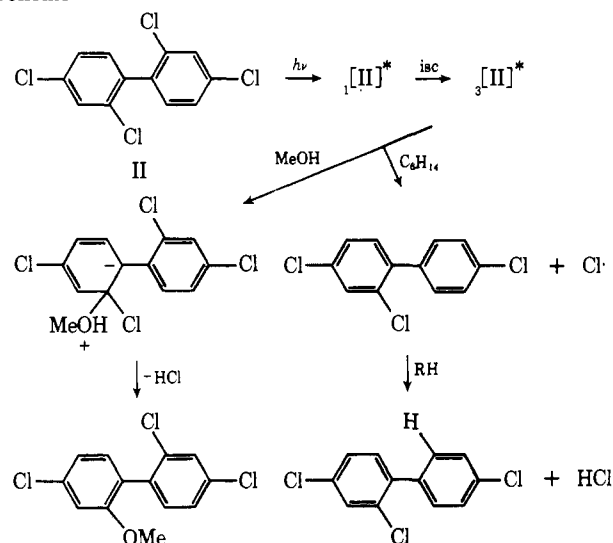
solutions of this PCB irradiated with varying concentrations (Q) of quencher showed decreased k values:

$k \times 10^7 M \text{ sec}^{-1}$	$Q, 10^{-3} M$
1.80	0
1.52	2.69
1.21	5.58
1.04	8.07
0.62	13.45

The fact that oxygen, also a triplet quencher, reduces the rate suggests the same conclusion.

The intermediate involved in this reaction appears to be similar to that observed by Kharasch (1968) in the photo-reaction of iodobiphenyl in benzene. The main product observed was terphenyl, arising from free radical attack on the solvent. In other solvents biphenyl is formed by hydrogen abstraction. In both cases a free radical type of intermediate has been invoked, although no iodine scavenging was observed. It is probable that PCB's yield similar "free" radical intermediates when photolyzed in hexane or methanol solutions. This would explain the occurrence of dechlorination products. Methoxylated products must

Scheme I



form through a different mechanism, probably involving nucleophilic attack by methanol and subsequent elimination of chlorine and/or hydrochloric acid. This mechanism would explain the hydroxylated products obtained by Hutzinger and coworkers (1971) in the photolysis of PCB's in aqueous dioxane solutions (see Scheme I).

CONCLUSIONS

The photolysis of polychlorinated biphenyls at wavelengths greater than 290 nm indicates the environmental significance of such nonbiological degradations. The determination of photoproduct structure and reaction rates is intimately related to the mechanism of the reaction. The presence of methanol substitution products suggests the possibility of degradative "handles" which can be introduced photochemically to compounds which are otherwise stable to most biological metabolic pathways. The effects of different chlorine substitution patterns upon reaction rates and the resulting products are of ecological significance.

At present we are investigating other photochemical properties of these compounds.

LITERATURE CITED

- Acker, L., Schulte, E., *Naturwissenschaften* 57, 497 (1970).
 Beaven G. H., *J. Chem. Soc.* 4637 (1956).
 Biros, F. J., Walker, A. C., Medbery, A., *Bull. Environ. Contam. Toxicol.* 5, 317 (1970).
 Braunton, P., *J. Chem. Soc. Perkin-Trans.* 2 138 (1972).
 Crosby, D. G., Tutass, H. O., *J. Agr. Food Chem.* 14, 596 (1966).
 Edwards, R., *Chem. Ind.* 1340 (1971).
 Fugita, S., *Fukuoka Igaku Zasshi* 62, 30 (1971).
 Hoopingarner, R., et al., *Environ. Health Pers.* 1, 155 (1972).
 Hutzinger, O., Safe, S., Zitko, V., *Bull. Environ. Contam. Toxicol.* 6, 160 (1971).
 Kharasch, N., *Angew. Chem. Int. Ed. Engl.* 7, 36 (1968).
 Kornblum, N., *J. Amer. Chem. Soc.* 74, 5782 (1952).
 Mitchell, L. C., *J. Ass. Offic. Agr. Chem.* 44, 643 (1961).
 Ruzo, L. O., Zabik, M. J., Schuetz, R. D., *Bull. Environ. Contam. Toxicol.* 8, 217 (1972).
 Safe, S., Hutzinger, O., *Nature (London)* 232, 641 (1971).
 Taylor, E. C., *J. Amer. Chem. Soc.* 92, 3520 (1970).
 Tsutsui, M., *J. Amer. Chem. Soc.* 79, 3062 (1957).
 Vos, J. G., *Toxicol. Appl. Pharmacol.* 17, 656 (1970).
 Wagner, P. J., *J. Amer. Chem. Soc.* 89, 2820 (1967).

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Solubility and Molecular Structure of 4-Amino-3,5,6-trichloropicolinic Acid in Relation to pH and Temperature

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The solubility of 4-amino-3,5,6-trichloropicolinic acid (picloram) was investigated at pH 0.20, 1.10, 2.0, 2.8, 4.2, and 4.7, and at 10, 20, 30, and 40°. The pK_a values at these temperatures and the molar heats of solubility, ΔH_{sol}° , of picloram at these pH's are reported. Explanation is offered for the variation of solubility of picloram with equilibrium pH and temperature. Dominant structural species and equilibria involved at various pH ranges are suggested and elucidated. Infrared studies of picloram at different pH's show that the intensities of the absorption bands at

2600 and 2650 cm^{-1} , the stretching vibration of $=N^+H$, increase inversely with pH. Existence of a number of solid structures of picloram was suggested. The possible formation of the zwitterion and cationic species at low pH is speculated. These findings are discussed as applied to picloram absorption on soil and its potential as an environmental contaminant. Also discussed is application of the values of ΔH_{sol}° as a correction of solubility-temperature effect on the standard enthalpy of pesticide adsorption processes.

Picloram (4-amino-3,5,6-trichloropicolinic acid) has been introduced as a herbicide for controlling weeds in ce-

real grains including wheat, oats, rice, and corn (Gantz and Warren, 1966; Haagsma and Wiffen, 1966). Broadcast application of a mixture of picloram and 2,4,5-T has been very effective in controlling undesirable woody species, broadleaf weeds, and brushes infesting over 88 million

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acres of Texas rangelands (Hoffman, 1971). Picloram is highly active at low application rate (Hamaker *et al.*, 1963) but relatively nontoxic to animal species (Lynn, 1965). Its resistance to degradation in the environment, however, ranks next to that of the chlorinated hydrocarbons, posing some pollution implications. Though picloram is rather mobile in some soils (Biggar and Cheung, 1971) it persists in other soils long enough to accumulate in high concentrations that thereby eliminate some desirable grass from pastures (McCarty and Scifres, 1968) because of its ready absorption and translocation by plants (Sharma *et al.*, 1971). The fate of herbicides in soil, including their susceptibility to microbial and chemical decomposition and other losses, is greatly influenced by their mobility and adsorption in soil, which are affected, in turn, by their solubilities (Davis *et al.*, 1954; Hilton and Yuen, 1963; Mills and Biggar, 1969), the soil pH (Hurt *et al.*, 1958), and the soil temperature (Mills and Biggar, 1969; Sheets *et al.*, 1964).

Picloram is an amino- and chlorine-substituted picolinic acid. However, in spite of the presence of the amino group, amphoteric property was not observed (Hamaker *et al.*, 1968). This is not surprising because of the electron-withdrawing property of the carboxyl and chlorine groups, which reduce the basicity of both the amino and pyridine nitrogens. Some picolinic acids could exist in its unionized, anionic, cationic, and dipolar forms (Katritzky and Lagowski, 1963), depending on the medium pH. From structural consideration, it is possible that picloram would exist as the unionized acid (or molecular species), the deprotonated (or anionic) species, the cationic species, and in zwitterion (dipolar) form, depending on solution pH. The latter two forms may exist at more strongly acidic media. These postulated structures are contained in Table I. The strength of association of organic chemicals (glycerol, nitromethane, acetonitrile, and nitrobenzene) with mineral surfaces has been shown to correlate directly with polarity of the chemicals from an X-ray diffraction study of the interlayer spacings (d_{001}) of montmorillonite clay (Barshad, 1952). The cationic and the more polar zwitterion species will no doubt interact more strongly with the negatively charged clay surface. If these two species exist in certain natural soil media, picloram will be protected from chemical and microbial degradation.

This paper reports the solubilities of picloram at various pH's and temperatures. The possibility of the existence of the dipolar and cationic structures of the chemical is speculated from the results of solubility and infrared spectroscopy studies. The structural relationship of the chemical to its solubility at various pH's and temperatures is discussed, elucidating its varied pollution implications, persistence, and behavior in different soils.

EXPERIMENTAL SECTION

Apparatus. Absorbance was measured with a Carl Zeiss spectrophotometer, PMQII, and infrared studies were done with a Beckman IR-10 infrared spectrophotometer. Solubility experiments were equilibrated in a 50-gal constant-temperature bath (Catalog no. 4-8605) equipped with a shaker (Catalog no. D1-62073), both manufactured by American Instrument Co., Inc. The temperature control of the bath was within $\pm 0.5^\circ$. The pH's were measured by a Beckman Expandomatic pH meter and a Corning combination electrode (Catalog no. 476051), except when otherwise noted. The instrument was standardized with Beckman pH buffers. Ultracentrifugation was performed on a Sorvall refrigerated-automatic centrifuge with a temperature control within $\pm 1^\circ$. It was equipped with an SS-34 rotor capable of developing a maximum centrifugal force of $34,800 \times g$.

Reagents. Analytical grade 4-amino-3,5,6-trichloropicolinic acid was supplied by Dow Chemical Co. Its purity

Table I. Various Possible Species of Picloram in Solution

Structure	Name	Abbreviated symbol
	Solid picloram	HP(solid)
	Anionic	P ⁻
	Dissolved picloram	HP _s
	Dipolar	H ⁺ P ⁻
	Cationic	HPH ⁺

was specified by Dow as greater than 99% by weight. All the chemicals used were reagent grade.

Experimental Procedures. Solubility Studies. Excess pure picloram solid was placed in a 4½-in. demuth screw-capped (tin foil-lined) vial. Distilled water was added and pH was adjusted by either hydrochloric acid or sodium hydroxide (various concentrations used depending on desired pH). The vials were allowed to warm to about 20° above the desired equilibrium temperature. Then they were equilibrated with gentle shaking for 20 hr at the desired temperature in a constant temperature water bath. Blank samples (without picloram) were treated identically. At the end of equilibration, the solids were allowed to settle. A small volume (1-5 ml) of the supernatant solution was centrifuged for 2 hr at 15,000 rpm at the same equilibrated temperature. The size of the undissolved particles was calculated (Bowman *et al.*, 1960). Particles with diameter greater than 88 Å were removed by the ultracentrifugal force of $30,000 \times g$. A method slightly different from the above was also attempted. By this method, solids were shaken in the vials at the desired temperature (without initial heating above this temperature) until there was no change in the concentration of the supernatant solution. Results obtained from both methods were within 4% of each other, and the first method was used to obtain the values reported. The concentration of picloram in the supernatant solution was analyzed by a colorimetric method (Cheng, 1969). The absorbance at 400 nm was

Table II. Solubility of Picloram at Various pH's and Temperatures and Its Molar Heats of Solubility

pH	10°, 10 ³ × M ^a	20°, 10 ³ × M	30°, 10 ³ × M	40°, 10 ³ × M	ΔH° _{sol} , kcal/mol
0.20 ± 0.05	0.182 ±0.017	0.305 ±0.003	0.495 ±0.008	0.89 ±0.12	9.2 ± 0.6
1.10 ± 0.05	0.162 ±0.004	0.260 ±0.020	0.451 ±0.046	0.824 ±0.017	9.3 ± 0.2
2.0 ± 0.1	0.369 ±0.004	0.567 ±0.025	0.85 ±0.05	1.31 ±0.02	7.5 ± 0.2
2.8 ± 0.1 (H ₂ O) ^b	1.967 ±0.017	2.26 ±0.13	2.83 ±0.29	3.29 ±0.06	3.1 ± 0.2
4.2 ± 0.1	92.1 ±1.4	81.0 ±4.0	88.6 ±3.5	88.5 ±6.6	0 ± 0.44
4.7 ± 0.2	349.7 ±0.3	308.9 ±3.5	340.6 ±1.5	324.0 ±4.4	0 ± 0.35

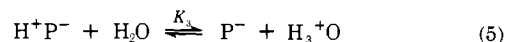
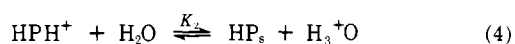
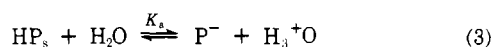
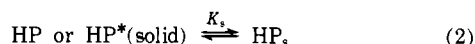
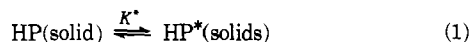
^a Mol/l. ^b Directly in distilled water.

measured against the background solution contained in a pair of matched quartz cells with a 1-cm path length. The background solution was prepared from the blank samples and treated identically as the picloram solution for color development. Lambert-Beer's law was followed only up to $8.28 \times 10^{-5} M$ (20 ppm). Picloram solutions with higher concentrations were diluted volumetrically with distilled water prior to chemical reactions for color development. The molar absorptivity of the diazonium salt of picloram at 400 nm (ϵ_{400nm}) is $(5.8 \pm 0.4)10^3 M^{-1} cm^{-1}$.

Infrared Studies. A saturated solution of picloram (acid) was prepared in the dark. Thirty milliliters of the supernatant solution was transferred to a 50-ml beaker and adjusted to the desired pH with dilute HCl or NaOH. The solution was centrifuged at 15,000 rpm for 30 min, and the supernatant solution was evaporated to dryness at room temperature in a vacuum desiccator. Infrared results were identical when the solution was evaporated at 75° in a forced-fan oven. One milligram of the resulting dried picloram was added to 100 mg of KBr (Beckman IR grade, oven-dried at 110° for 2 hr), ground with a marble mortar and pestle, and mixed in a vibrator for 3 min. The mixture was then pressed (under 18,000 lb/in.²) into a pellet for analysis. Spectra for the region 4000-600 cm⁻¹ were obtained on a Beckman IR-10 spectrophotometer.

RESULTS AND DISCUSSION

Solubility Studies. When picloram in excess is dissolved in water, the following possible equilibria exist.



The symbol HP*(solids) represents other possible solid structures other than HP(solid). Evidence of their existence is discussed under "Infrared Studies" later in this report. The other symbols in the equations and their corresponding structures are represented in Table I.

The pK_a value of picloram (eq 3) at 25° was reported to be 4.1 (Hamaker *et al.*, 1968). We have determined the pK_a values to be 3.43, 3.42, 3.39, and 3.36 at 10, 20, 30, and 40°, respectively, by titrating an aqueous solution of picloram against a carbonate-free standard KOH solution. A pK_a value of 3.4 at 25° has also been reported (Volk and Kuo, 1970). The standard enthalpy of the acid dissociation

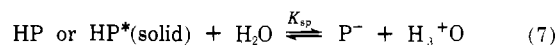
process, ΔH° , was calculated by the integrated form of the van't Hoff equation (plotting $\ln K_a$ vs. $1/T$)

$$\ln(K_{a2}/K_{a1}) = -\Delta H^\circ(1/R)(1/T_2 - 1/T_1) \quad (6)$$

where K_{a1} and K_{a2} are, respectively, the acid dissociation constants at temperatures T_1 and T_2 . The recorded error in ΔH° , δH° , corresponds to one-fourth the limit of uncertainty in the $\ln K_a$ vs. $1/T$ plots (Livington, 1948). The value of ΔH° for equilibrium K_a (eq 3) was calculated to be 0.97 ± 0.27 kcal/mol.

The solubility, C_0 , of picloram was studied at six pH's: 0.20, 1.10, 2.0, 2.8, 4.2, and 4.7. Table II contains the solubilities at 10, 20, 30, and 40°. The solubility was not affected by ionic strength up to 0.5 M in KCl at the temperatures studied. The molar heats of solubility (or the latent heat of solution) of picloram, ΔH°_{sol} , at various pH's were calculated by eq 6 using solubilities, C_0 , at T_1 and T_2 . Figure 1 is a plot of the natural log of solubility ($\ln C_0$) vs. the reciprocal of the absolute temperature ($1/T$) at various pH's.

Above pH 4.2, solubility is not affected by temperatures between 10 and 40°, and the value of ΔH°_{sol} is practically zero. At pH's of 4.2 and 4.8, respectively, 86.3 and 95.2% of the picloram molecules are in the anionic form. (These were calculated based on $pK_a = 3.4$ at 25°. The maximum difference of the calculated percentages from pK_a 's at 10 and 40° was less than 2.6% for all the systems reported.) This result indicates that the equilibrium between solid picloram and the dissolved anionic species, or the solubility product, K_{sp} , is not temperature dependent. The equilibrium represented by K_{sp} is the combined equilibria K_s and K_a , where K_{sp} is the product of K_s and K_a .



At pH 2.8 and below, the solubility of picloram increases with temperature and the solubility processes have positive ΔH°_{sol} values. The percentages of the protonated species (molecular plus dipolar plus cationic) at pH 2.8, 2.0, 1.10, and 0.20 are, respectively, 79.9, 96.2, 99.5, and 99.9 (based on $pK_a = 3.4$ at 25°). At higher temperatures, the protonated species are deprotonated and the formation of the anionic species is favored. The concentration of the protonated species is depleted, which is supplemented through equilibrium K_s when more solid picloram molecules are dissolved or solvated. At the new equilibrium, the overall soluble picloram species (anionic and protonated) increases. It is also observed that the values of ΔH°_{sol} increase inversely with pH (Table II). At lower pH, the protonated species become more abundant and the solubility-temperature effect becomes more intense, resulting in an inverse relationship of ΔH°_{sol} with pH.

The solubility of picloram decreases with pH (until pH 1.1) at any one temperature. This is expected for a weak

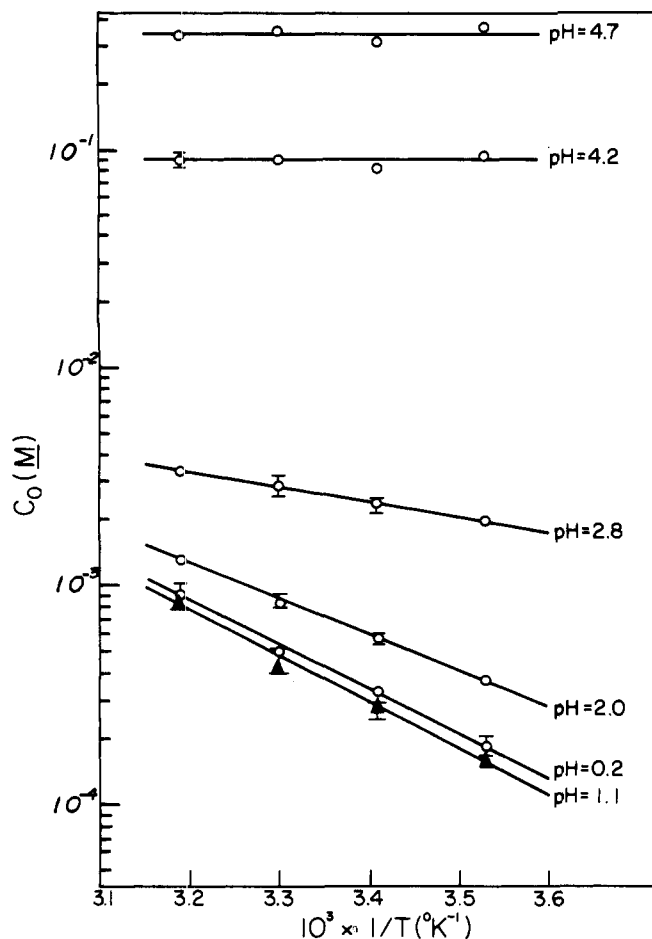


Figure 1. Plots of the natural log of the solubility ($\ln C_0$) vs. the reciprocal of the absolute temperature ($1/T$).

organic acid. The total solubility of picloram can be derived from eq 3, 4, and 5.

$$\begin{aligned} \text{total solubility} &= [\text{HP}_s] + [\text{P}^-] + [\text{HPH}^+] + [\text{H}^+\text{P}^-] \\ &= [\text{HP}_s](1 + K_a/K_3 + K_a/[\text{H}_3^+\text{O}] + \\ &\quad [\text{H}_3^+\text{O}]/K_2) \quad (8) \end{aligned}$$

The total solubility thus depends on the concentrations of H_3^+O and HP_s species. The concentration of the latter is also pH dependent. While the values of K_2 , K_3 , and $[\text{HP}_s]$ are not known, it is difficult to assess the pH effect on solubility from eq 8. Suffice it to note that the terms $K_a/[\text{H}_3^+\text{O}]$ and $[\text{H}_3^+\text{O}]/K_2$ relate to $[\text{H}_3^+\text{O}]$ in opposite directions. If $K_3 \gg K_a$ and $K_2 \leq 1$, these two terms are significant at certain pH levels throughout the pH range studied.

At pH 0.20, the solubility is slightly higher than at pH 1.10. This could have been caused by the $[\text{H}_3^+\text{O}]$ effects discussed above. At pH 0.20, 99.9% ($\text{p}K_a = 3.4$ at 25°) of the picloram species is in the protonated form. It is possible that the H^+P^- and HPH^+ species are more abundant and that they are more soluble in water than the molecular form. The total solubility of picloram, after eliminating the contribution from P^- (0.1% of all the species) by combining eq 3 and 5, has the form

$$\begin{aligned} \text{total solubility} &= [\text{HP}_s] + [\text{H}^+\text{P}^-] + [\text{HPH}^+] \\ &= [\text{HP}_s](1 + K_1/K_3 + [\text{H}_3^+\text{O}]/K_2) \quad (9) \end{aligned}$$

Equation 9 shows a direct relationship of solubility with $[\text{H}_3^+\text{O}]$.

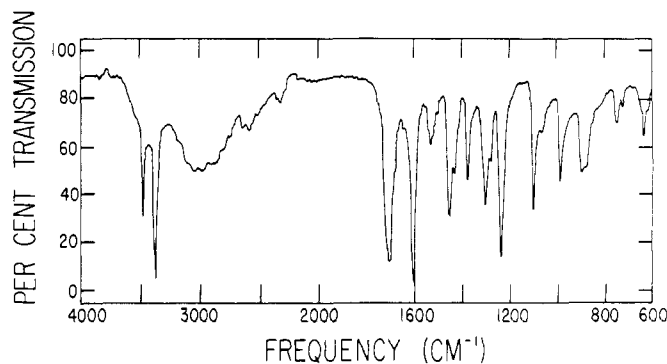


Figure 2. Infrared spectrum of 4-amino-3,5,6-trichloropicloramic acid recrystallized from distilled water.

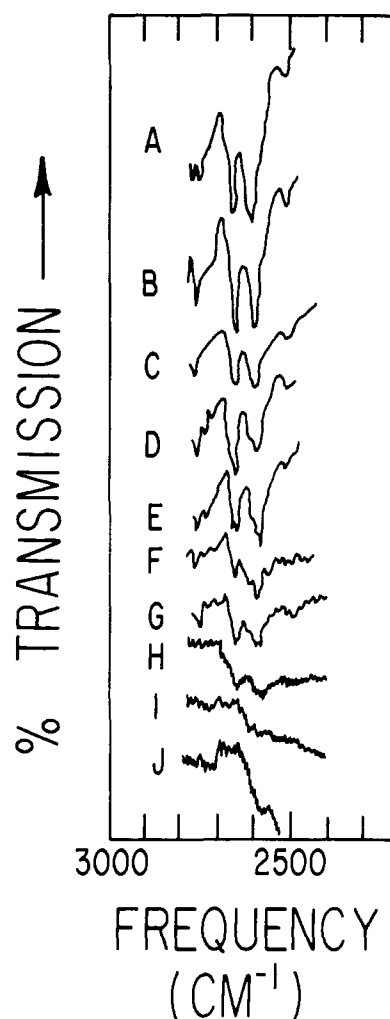


Figure 3. Intensity of the stretching vibration of ($=\text{N}^+\text{H}$) at 2600 and 2650 cm^{-1} at the following pH's: (A) recrystallized from HCl (< -1); (B) -1 ; (C) 0.05 ; (D) 1 ; (E) 2 ; (F) 2.7 ; (G) 4 ; (H) 5 ; (I) 6 ; and (J) from excess NaOH (> 9).

From the solubility results, one can conclude that picloram exists in various forms in the aqueous medium. The possibility of the existence of the dipolar and cationic species is greater at lower pH.

Infrared Studies. Infrared spectra were measured in the region $4000\text{--}600 \text{ cm}^{-1}$. Figure 2 is the infrared spectrum (KBr pellet) of picloram recrystallized from distilled water. The vibration frequencies of the bands of picloram are similar at different pH's except as noted below. Spectra of picloram, recrystallized from solutions with an ini-

tial pH of -1 or lower (pH calculated from H_3^+O), have a very broad intense bonded O-H stretching absorption centered on 3000 cm^{-1} , which is characteristic of the unionized carboxyl group. Its intensity gradually becomes lower from samples recrystallized from solutions with an initial pH of 0.05 and 1 and becomes weak to very weak at an initial solution pH of 2 and 2.7, and finally vanishes at an initial solution pH higher than 2.7. The bands at 2600 and 2650 cm^{-1} have been assigned to the stretching vibrations of $=N^+H$ (Rao, 1963). The intensity of these two bands decreases inversely with pH, finally disappearing at pH higher than 4 (Figure 3). (The pH of the solution prior to recrystallization was slightly different from the initial pH due to evaporation.) The results from infrared studies seem to indicate that various solid structures occur at different pH's. We may speculate that the cationic and dipolar structures also occur. Their percentage is larger at lower pH's.

Application of Findings to Adsorption Process. The possibility of the existence of the zwitterion and cationic structures at low pH and the pH-dependent solubility of picloram has some implication on the contamination of the herbicide in the soil. On the basis of solubility, one would expect that more picloram molecules will be adsorbed at a lower pH because the adsorbed phase is energetically favorable. Furthermore, the charge of the picloram molecules is either neutral (molecular form) or dipolar or positive (cationic), or a combination of all. Its adsorption on a negatively charged surface (clay platelets) is enhanced as a result of the more favorable electrostatic interaction. Reported results (Biggar and Cheung, 1973; Hamaker *et al.*, 1968) indicate that adsorption of picloram is increased with decreasing pH in a number of soil-water systems.

Natural mineral soils have a large range of soil pH between 3 and 11, while the more productive agricultural soils have pH between 5 and 9. Because of the suspension effect, the actual pH of the clay mineral surface may be one or two pH units below that of the soil solution (Mortland and Raman, 1968; Swoboda and Kunze, 1968) for acidic soils. Thus, the behavior of picloram varies with the soil pH. When picloram is more mobile (alkaline soils), it is more reactive, more easily degraded chemically and microbiologically, more available to plants, and has a better chance to leach through the soil and contaminate ground and well water. When it is more adsorbed and less mobile (acidic soils), the reverse is true.

Thermodynamic parameters have been used to describe the adsorption processes and adsorption mechanisms of pesticides on soils. The solubility-temperature effect was observed to be important in the adsorption processes. Mills and Biggar (1969) demonstrated that the apparent exothermic adsorption process of lindane on various adsorbents became endothermic after correction for the solubility-temperature effect of lindane. The uncorrected standard enthalpy of adsorption, ΔH°_{Ad} , is obtained from a plot of $\ln(C_s/C)$ vs. $1/T$ according to the van't Hoff equation, where C_s/C is the thermodynamic distribution coefficient of adsorption obtained by extrapolating to zero C_s . The conventional method of obtaining the corrected ΔH°_{Ad} , or ΔH°_{CAd} , is by plotting $\ln[C_s/(C/C_0)]$ vs. $1/T$, where C_0 is the solubility of the herbicide at temperature T and at the same pH as the adsorption process (Mills

and Biggar, 1969). With the aid of the values of ΔH°_{sol} , ΔH°_{CAd} is obtained simply as the sum of ΔH°_{sol} and ΔH°_{Ad} . A much simplified derivation is shown below. According to the van't Hoff equation

$$\begin{aligned} [-\Delta H^\circ_{CAd}](1/R)(1/T_2 - 1/T_1) = \\ \ln [C_{S2}/(C_2/C_{02})] - \ln [C_{S1}/(C_1/C_{01})] = \\ [\ln (C_{S2}/C_2) - \ln (C_{S1}/C_1)] + \\ [\ln C_{02} - \ln C_{01}] = \\ \{[-\Delta H^\circ_{Ad}] + [-\Delta H^\circ_{sol}](1/R)(1/T_2 - 1/T_1)\} \quad (10) \\ \text{or } \Delta H^\circ_{CAd} = \Delta H^\circ_{Ad} + \Delta H^\circ_{sol} \quad (11) \end{aligned}$$

We have attempted this approach to the picloram-Panoche-water adsorption process at pH 1.2 (HCl) (Biggar and Cheung, 1973). The values of ΔH°_{CAd} obtained were identical to those calculated by the conventional method. For systems with equilibrium pH higher than 4, no correction is needed, since ΔH°_{sol} is practically zero.

ACKNOWLEDGMENT

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LITERATURE CITED

- Barshad, I., *Soil Sci. Soc. Amer. Proc.* **16**, 176 (1952).
 Biggar, J. W., Cheung, M. W., unpublished results, 1971.
 Biggar, J. W., Cheung, M. W., *Soil Sci. Soc. Amer. Proc.* **36**(6), Nov-Dec (1973).
 Bowman, M. C., Acree, F., Jr., Corbett, M. K., *J. Agr. Food Chem.* **8**, 406 (1960).
 Cheng, H. H., *J. Agr. Food Chem.* **17**, 1174 (1969).
 Davis, F. L., Selman, F. L., Davis, D. E., *Proc. S. Weed Conf.* **7**, 205 (1954).
 Gantz, R. L., Warren, L. E., *Down Earth* **22**(1), 13 (1966).
 Haagsma, T., Wiffen, E. E., *Down Earth* **21**(4), 22 (1966).
 Hamaker, J. W., Goring, C. A. I., Youngson, C. R., "Organic Pesticides in Environment," *Advances in Chemistry Series 60*, American Chemical Society, Washington, D. C., 1968, pp 23-37.
 Hamaker, J. W., Johnston, H., Martin, R. T., Redemann, C. T., *Science* **141**, 363 (1963).
 Hilton, H. W., Yuen, Q. H., *J. Agr. Food Chem.* **11**, 230 (1963).
 Hoffman, G. O., *Down Earth* **27**(2), 17 (1971).
 Hurtt, W., Meade, J. A., Santelmann, P. W., *Weeds* **6**, 425 (1958).
 Katritzky, A. R., Lagowski, J. M., in "Advances in Heterocyclic Chemistry," Vol. 1, Katritzky, A. R., Ed., Academic Press, New York, N. Y., 1963, p 404.
 Livingston, R., "Physical Chemical Experiments," 3rd ed, MacMillan Co., New York, N. Y., 1948, p 44.
 Lynn, G. E., *Down Earth* **20**(4), 6 (1965).
 McCarty, M. K., Scifres, C. J., *Weed Sci.* **16**, 443 (1968).
 Mills, A. C., Biggar, J. W., *Soil Sci. Soc. Amer. Proc.* **33**, 210 (1969).
 Mortland, M. M., Raman, K. V., *Clays Clay Miner.* **16**, 393 (1968).
 Rao, C. N. R., "Chemical Application of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963, p 246.
 Sharma, M. P., Chang, F. Y., Vanden Born, W. H., *Weed Sci.* **19**, 349 (1971).
 Sheets, T. J., Kearney, P. C., Smith, J. W., *Weeds* **12**, 83 (1964).
 Swoboda, A. R., Kunze, G. W., *Soil Sci. Soc. Amer. Proc.* **32**, 806 (1968).
 Volk, V. V., Kuo, E. C. Y., Contributing report from Oregon State University to Western Regional Research Project W-82, "Pesticide Mobility and Degradation in Soil-Water Systems," presented in Denver, Colorado, Dec 2-3, 1970.

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