Hexazinone: Polarographic Reduction and Adsorption on Lignin

Marina Privman, Elinore B. Rupp, and Petr Zuman*

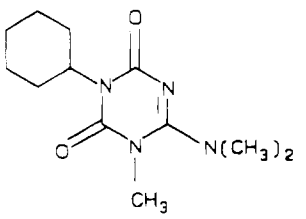
Department of Chemistry, Box 5810, Clarkson University, Potsdam, New York 13699-5810

Hexazinone [3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione] (**I**) is reduced in acidic media at the dropping mercury electrode in two two-electron steps. The first step corresponds to a reduction of a protonated azomethine bond which is complicated at pH 2–4 by the establishment of a hydration–dehydration equilibrium. Measurement of the first wave at pH 3.7 is suitable for analytical purposes and was used for following the adsorption of hexazinone on lignin. In comparison with acifluorfen, thiram, and DCNA, which had been studied earlier, hexazinone is less strongly adsorbed and is rapidly desorbed.

Keywords: *Lignin; hexazinone; adsorption; polarography*

INTRODUCTION

The active component of Velpar weed killer (E. I. du Pont de Nemours & Co.), used for control of many annual and perennial weeds and plants in fields, forests, and aquatic systems, is hexazinone [3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione] (**I**). In forestry it is used as a selective herbicide



(**I**)

for site preparation, for release of conifers, and as a nonselective herbicide for weeds and woody plants (*Pesticide Background Statements*, 1985). The primary mechanism of its uptake by plants is absorption from soil by roots. As forest litter and soil contain considerable amounts of lignin, it was of interest to investigate the binding of hexazinone on lignin and the release of the lignin bound compound into aqueous solutions to be able to apply the minimum amount of pesticide for effective bioavailability. To follow the binding of hexazinone on lignin, an analytical method had to be developed which would allow the observation of changes in the hexazinone concentration in systems containing smaller and larger solid particles, as well as the smaller water soluble fragments of lignin.

Our previous experience with studies of the binding of both organic (Rubio *et al.*, 1979; Paden *et al.*, 1983; Zuman *et al.*, 1988; Ainso *et al.*, 1988; Rupp and Zuman, 1992; Rupp *et al.*, 1992) and inorganic (Kulik *et al.*, 1986; Wieber *et al.*, 1988) species by lignin indicated that polarography is well suited for this purpose. Polarographic determinations are possible in a wide range of concentrations [in direct current (dc) polarography from about 1×10^{-5} M to 1×10^{-3} M, in differential pulse polarography (DPP) from about 1×10^{-7} M to 1×10^{-3} M solutions] even in the presence of dispersed particles. As only a brief comment concerning the polarographic reduction of hexazinone has been reported in the literature (Polák and Volke, 1983), it was first necessary to carry out basic electrochemical studies to elucidate at least the principal electrochemical and chemical processes involved in the reduction. Such understanding is essential for the development of a reliable analytical procedure and for finding the optimal conditions for determination of hexazinone.

EXPERIMENTAL PROCEDURES

Instrumentation. The dc current voltage curves were recorded using a Sargent-Welch Mark 4001 polarograph with a controlled drop time of 1 s or a EC 225^{1A} voltammetric analyzer and 7424MT X-Y-T recorder (IBM Instruments, Inc.). DPP curves were recorded using the Sargent-Welch polarograph with excitation signal $\Delta e = 50$ mV and a controlled drop time (1 s). The dropping mercury electrode used with the Sargent-Welch polarograph had $m = 1.89$ mg/s and $t_1 = 3.85$ s at $h = 83$ cm in a 0.1 M KCl at 0.0 V (SCE). The curves were recorded with $h = 91$ cm. Two dropping mercury electrodes were used with the EC 225^{1A}: One was a straight capillary with $m = 3.01$ mg/s and $t_1 = 2.9$ s at $h = 73.5$ cm, the other was a Smoleŕ (Smoleŕ, 1954) capillary bent by 90°, with $m = 0.64$ mg/s and $t_1 = 1.8$ s at $h = 72$ cm in a 0.1 M KCl at 0.0 V (SCE). Polarographic studies were conducted in a Kalousek cell using a liquid junction separated saturated calomel electrode as a reference.

pH measurements were carried out with a PHM 84 Research pH meter (Radiometer) with a G202B glass electrode and a K422 saturated calomel electrode, both from Radiometer. UV absorption spectra were recorded with a Perkin-Elmer spectrophotometer Mark 559.

Chemicals and Solutions. Hexazinone (Velpar, 98%) was obtained from Chem Services. Stock solutions of 0.01–0.02 M hexazinone were prepared by dissolution in dimethylformamide or in acetonitrile. Fresh stock solutions were prepared weekly and stored in brown bottles at room temperature. No measurable change in concentration of the stock solution was observed for at least 20 days.

Chemicals used for preparation of the buffers were analytical or reagent grade and used as supplied. Sodium hydroxide solutions and (0.1 M) sulfuric acid solutions (0.01–5.0 M) were used, with sodium sulfate added to keep the ionic strength to 0.3 or 0.6 in solutions containing less than 0.1 M H_2SO_4. Acetate buffers were prepared by mixing solutions of acetic acid and sodium acetate in varying proportions, keeping the total analytical concentration of acetic acid 0.2 M. To prepare phosphate buffers of pH 1.5–3.5, solutions of potassium dihydrogen phosphate were titrated with phosphoric acid to the desired pH, keeping the concentration of phosphate 0.05 M. In the preparation of phosphate buffers of pH 6.3–7.8, solutions of potassium dihydrogen phosphate were titrated by sodium hydroxide, keeping the total phosphate concentration 0.05 M. Similarly, borate buffers of pH 8.3–10.3 were

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prepared by titrating a solution of boric acid with sodium hydroxide keeping the total concentration of boric acid 0.05 M.

Solutions containing 30% v/v ethanol used in the investigation of the reduction mechanism were prepared in an analogous way. The "pH" value of each solution containing mixed solvents was measured with a glass electrode standardized using commercial aqueous buffers. Hence, the "pH" values quoted are only relative and the actual activity of the hydrogen ions will also depend on the nature of the buffer used. All solutions were purged with nitrogen for at least 2 min before recording the current voltage curves.

Preparation of Lignin Samples. One commercial and three natural lignins were used in this study. All of the materials, except one, were washed.

Indulin ATR-CK1 from Westvaco was prepared from precipitated softwood kraft lignin by heat coalescence and spraying: C_9 formula, $C_9H_{8.40}O_{2.39}S_{0.09}(OCH_3)_{0.79}$ (64.5% C, 5.82% H, 27.7% O, 1.6% S); unit weight 180; pH 3.68; ash 1.65%; acetone solubility 68.8%; carboxylic acid content 0.42 mol kg^{-1}; methoxy group content 4.50 mol kg^{-1}; phenolic hydroxide content 4.2 mol kg^{-1}. The surface area is about 100 m^2 g^{-1} (BET). This material (177 g) was washed twice with 1.5 L of distilled water and dried (L_1).

The natural materials were ground with a mortar and pestle and passed through a screen with 0.14 cm openings before being washed with distilled water.

The first natural material (P_1) came from the Clarkson University campus and was gathered from a rotten maple log lying on the surface of the ground. The material was of a light brown color, resembling indulin ATR-CK1, but still had some of the structure of the original wood. It was brittle and crumbled when pressed by fingers. It was brought to the laboratory in chunks and dried before grinding; 91 g of this material was dispersed in 1 L of distilled water for 2 days, filtered, and dried.

The second natural material (Q) was obtained from a rotten stump in the Manistee National Forest in Michigan and was similar in appearance to P_1. One portion (Q) was used directly after grinding and screening. For a preparation of a second specimen (Q_1), 57 g of the natural material were dispersed for 4–5 days in 1 L of distilled water, filtered, and dried.

The third natural material (R_1) was obtained from a rotten aspen log found lying on the ground in Postwood Park, Hannawa Falls, NY. After grinding and screening, 26 g of the powdery material was dispersed in 1.5 L of distilled water, filtered, and dried.

Calibration Curves for Adsorption Studies. For pH <2.5, the presence of smaller oligomers and fragments eluted from solid lignins caused the shape of the waves of hexazinone obtained by dc polarography to be distorted and the limiting current difficult to measure. Therefore, a 0.2 M acetate buffer with pH 3.7 was chosen for the adsorption studies.

Differential pulse polarographic (DPP) curves were preferred in the adsorption studies, because the dc polarographic curves were ill developed in the presence of soluble components of lignin (Figure 1). This is due partly to the presence of water soluble fragments of lignin (containing hydroxy and methoxy substituted aromatic aldehydes), which are reducible in the same potential range as hexazinone and furthermore can catalyze hydrogen evolution. We are aware (Rupp and Zuman, 1994) that generally DPP curves are more affected by surface activity of soluble lignin fragments than limiting currents obtained by dc polarography. However, these effects are less pronounced for hexazinone, which is reduced at more negative potentials where the adsorption plays a lesser role, than has been observed for pesticides containing a nitro group which are reduced at more positive potentials.

Aliquots of stock solution were gradually added to a 0.2 M pH 3.7 acetate buffer after it had been deoxygenated by a stream of nitrogen and DPP current-voltage curves were recorded. For concentrations 3.8×10^{-5} to 3.0×10^{-4} M, a single peak was observed at about −1.15 V, the height of which is a linear function of the concentration of hexazinone. Because an increasing volume of the stock solution was added to the buffer, the concentration of DMF varied between 0.25%

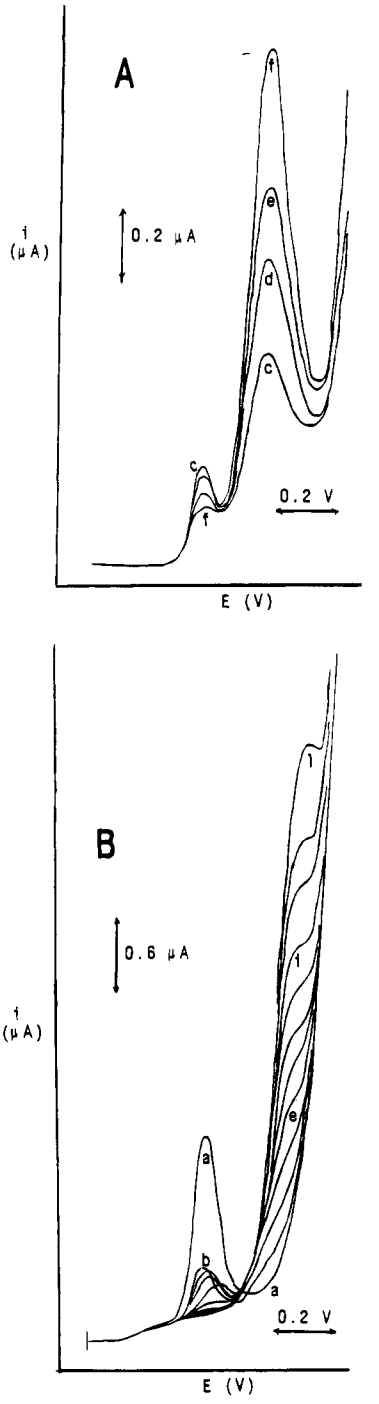


Figure 1. Dependence of DPP current-voltage curves on the concentration of hexazinone (A) in the absence and (B) in the presence of 0.3 g of lignin R_1 in 15 mL of solution. Starting concentration of hexazinone ($\times 10^{-5}$ M): (a) 0; (b) 3.9; (c) 7.8; (d) 11.7; (e) 15.7; (f) 19.7; (g) 23.5; (h) 27.4; (i) 31.3; (j) 35.3; (k) 39.2; (l) 47.1. Curves recorded from −0.4 to −1.4 V, t_1 = 1 s, ΔE = 50 mV, pH 3.7 acetate buffer.

and 1.96%. For concentrations of hexazinone higher than about 3.9×10^{-4} M, another peak appeared at about −1.23 V and its height was also a linear function of the concentration of hexazinone. Because the analysis is carried out in a pH range where the peak current strongly depends on pH, it is strongly recommended that a new calibration curve be constructed for each fresh stock and buffer solution.

Methodology of Adsorption Studies. Lignin (0.3 g) was dispersed in 15 mL of a 0.2 M aqueous acetate buffer in a 35 mL centrifuge tube. An attempt to study adsorption with $^1/_{10}$ the amount of lignin did not yield sufficiently reliable results. To the suspension of lignin, varying volumes (0.0375–0.900 mL) of the 0.01 or 0.02 M stock solution of hexazinone in

dimethylformamide were added. The tubes were placed on an Erbach 6460 Kahn shaker (38-mm stroke, 280 excursions/min) and shaken for approximately 21 h, unless otherwise stated. Subsequently, the tubes were placed in a IEC clinical centrifuge and centrifuged for 3 min at the maximum speed of 4500 rpm. The samples were decanted and the DPP current-voltage curves of the supernatant recorded. To ensure the highest accuracy of the determination of hexazinone, a parallel set of centrifuge tubes, containing various concentrations of hexazinone but without lignin, was treated in a similar manner.

To eliminate the possible effect of soluble and small lignin particles, "lignin wash" was separated from the larger particles using filtration with a Millipore type HA 0.45 μm filter. Lignin wash did not decrease measurably the concentration of hexazinone, as indicated by the unchanged limiting current in dc polarography. The small decrease in the height of the differential pulse polarographic peak was comparable with the decrease observed in the presence of other surfactants (Rupp and Zuman, 1994) and was attributed to the effect of surface active agents on the rate of the electrode process.

To test the effect of the concentration of DMF in the final solution, which varied from 0.5% to 6.5%, calibration curves of hexazinone were carried out in solutions where the concentration of DMF was kept at 6.5% and compared with curves obtained with DMF concentrations which varied in the studied range. The change of the slope of the $i = f(C)$ plot was negligibly small.

No measurable adsorption at the surface of the glass vials used was detected.

Methodology of Desorption Studies. A known weight of lignin was dispersed in 15 mL of 0.2 M pH 3.7 acetate buffer, and 0.38 mL of 0.016 M stock solution of hexazinone was added to correspond to an initial concentration of 3.9×10^{-4} M hexazinone. The suspension was equilibrated using a shaker for 20 h. After centrifugation, the supernatant was decanted, purged with nitrogen for 2 min, and analyzed for hexazinone concentration. To the wet residue, another 15 mL of pH 3.7 acetate buffer was added and shaken for another 20–24 h. The decanted supernatant was analyzed for hexazinone.

To follow the desorption as a function of pH, 0.3 g of aspen lignin (R_1) was dispersed in 15 mL of a pH 3.7 acetate buffer containing 3.9×10^{-4} M hexazinone and shaken for 20 h. After centrifugation, the concentration of hexazinone was determined and the amount of hexazinone bound on 0.3 g of lignin calculated. The solid residue was dispersed in 15 mL of 0.2 M acetate buffer of pH 3.7, 4.7, or 5.7 and shaken for 200 min, which was found to be sufficient to establish the adsorption–desorption equilibrium. The resulting suspensions were centrifuged and the pH adjusted to pH 3.7 by adding 0.8 mL of glacial acetic acid to buffer pH 4.7 or 1.5 mL of glacial acetic acid to buffer pH 5.7. The concentration of hexazinone in the resulting solutions was determined polarographically.

Two types of blanks were used to correct for possible reducible species in the lignin extract and for possible losses of hexazinone during the desorption procedure. For the first, a suspension of lignin in an acetate buffer pH 3.7 (without hexazinone) was handled in the same way as the samples with hexazinone and the current at −1.15 V measured. All data in the presence of hexazinone were corrected for this current. The second factor was eliminated by using a calibration curve based on measurements of peak currents of hexazinone in solutions handled by shaking, centrifugation and pH adjustment as above, only in the absence of lignin.

RESULTS AND DISCUSSION

DC Polarographic Reduction of Hexazinone. In aqueous solutions at pH >1, hexazinone is reduced in two two-electron steps, i_1 and i_2, the height of which decreases with increasing pH. The plot of the dependence of the limiting current on pH has a shape of a dissociation curve of a monobasic acid with an inflection point at about pH 4.3 (Figure 2). At pH 2–4, the smaller currents than would correspond to the theoretical curve (indicated by the solid line in Figure 2) are attributed to limited rate of dehydration of the hydrated hexazinone molecule, which predominates in solution. The half-wave potentials of waves i_1 and i_2 of hexazinone are practically pH-independent for pH < pK_a (about 1.2). In aqueous solutions, the slope of the two linear segments at pH > pK_a were about −0.07 V/pH for wave i_1 and −0.05 V/pH for wave i_2. Consequently, in aqueous solutions, the separation of waves i_1 and i_2 becomes poorer with increasing pH. For buffers containing 30% ethanol, the half-wave potentials of both waves i_1 and i_2 were shifted by about −0.07 V/pH (Figure 3). As a result, in the presence of the cosolvent the separation of waves i_1 and i_2 remains pH-independent.

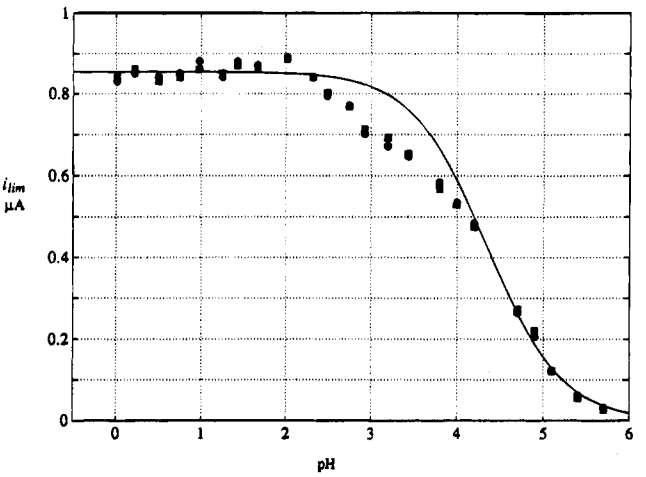


Figure 2. Dependence of dc polarographic limiting current of hexazinone on pH in aqueous solutions (1×10^{-4} M hexazinone in aqueous buffers containing 1% v/v DMF). (●) Experimental values for limiting current i_1; (□) values for limiting current i_2; (solid line) theoretical dissociation curve for a monobasic acid with pK' = 4.3; deviations between pH 2 and 4 discussed in text. v = 2 mV/s, m = 2.91 mg/s, t_1 = 2.95 s at h = 71 cm.

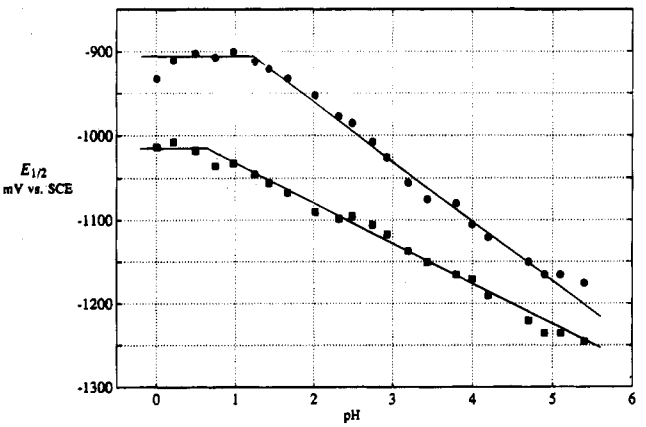


Figure 3. Dependence of half-wave potentials ($E_{1/2}$) of hexazinone on pH in aqueous solutions (1×10^{-4} M hexazinone in aqueous buffers containing 1% v/v DMF). (●) Values for wave i_1; (■) values for wave i_2. Line at pH >1.25 for i_1 is a least-squares fit for experimental data points with $dE_{1/2}/dpH$ = −0.071 V/pH. Line at pH >1 for i_2 is a least-squares fit with $dE_{1/2}/dpH$ = −0.048 V/pH. v = 2 mV/s, m = 2.91 mg/s, t = 2.95 s at h = 71 cm.

The better developed waves at pH 2 are the most suitable for analytical purposes. When various volumes of the 0.01 M stock solution of hexazinone in DMF were added to aqueous pH 2 buffer and, consequently, the concentration of DMF in the electrolyzed solution varied from 0.2% to 2% v/v, the total height $i_1 + i_2$ was a linear function of hexazinone concentration. The heights of

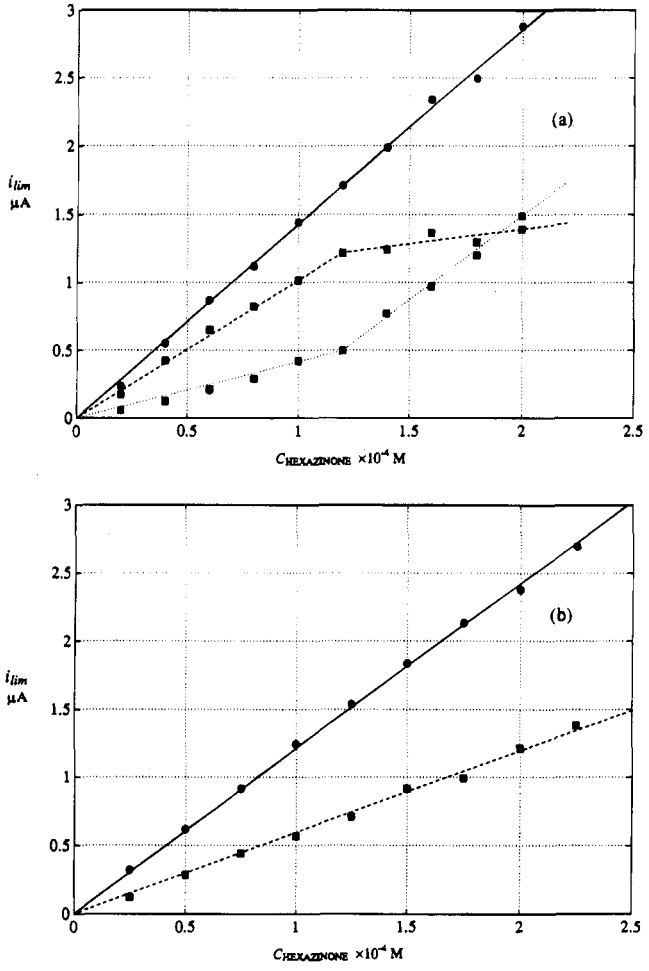


Figure 4. Dependence of limiting current on concentration of hexazinone in (a) solution of 0.03 M H_2SO_4 and 0.1 M Na_2SO_4 in water containing 0.25–2% v/v DMF, pH 2.0, and (b) solution of 0.01 M H_2SO_4 and 0.1 M Na_2SO_4 in water containing 30% v/v ethanol and 0.25–2.25% v/v DMF, "pH" 2.1. (●) Total wave-height ($i_1 + i_2$); (■) individual limiting currents; (dashed lines) i_1 (dotted lines) i_2. $v = 2$ mV/s, $m = 3.03$ mg/s, $t = 2.89$ s at $h = 74$ cm.

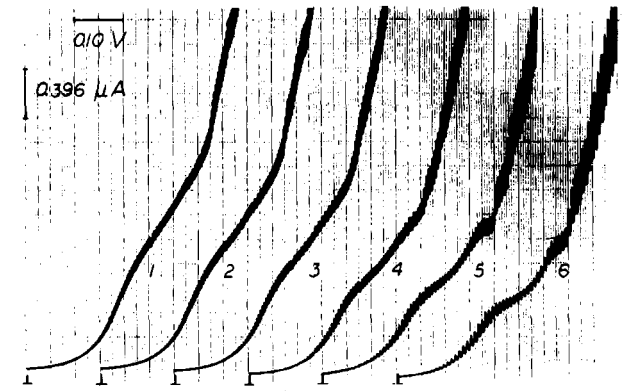


Figure 5. Dependence of dc polarographic current-voltage curves of hexazinone on the height of the mercury column (1.8×10^{-4} M hexazinone in aqueous solution of 0.02 M H_2SO_4 and 0.2 M Na_2SO_4 containing 1.8% v/v acetonitrile, pH 2.0). Mercury column heights: (1) 118 cm; (2) 104 cm; (3) 92.5 cm; (4) 72 cm; (5) 54 cm; (6) 42 cm. Curves were recorded from −0.8 V (SCE), $v = 3$ mV/s. Bent (90°) capillary, $m = 0.64$ mg/s, $t_1 = 1.8$ s at $h = 72$ cm at 0.0 V (SCE) in 0.1 M KCl.

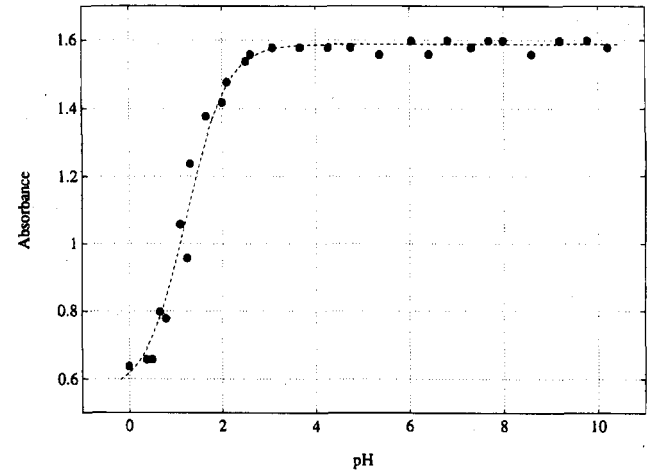


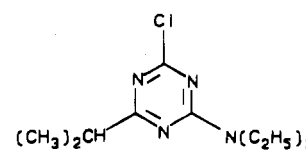
Figure 6. Dependence of absorbance of hexazinone at 244 nm on pH in aqueous solutions of buffers or sulfuric acid, containing 1×10^{-4} M hexazinone and 1% v/v DMF.

individual waves i_1 and i_2 have shown deviations from linear dependence on concentration for concentrations higher than about 1.2×10^{-4} M (Figure 4a). These deviations were attributed to an adsorption of the reduction product of hexazinone in aqueous solutions. In the presence of 30% v/v ethanol, both the first wave i_1 and the total wave height $i_1 + i_2$ were found to be a strictly linear function of hexazinone concentration from 2×10^{-5} to 2.25×10^{-4} M (Figure 4b).

At concentrations smaller than 1.2×10^{-4} M in aqueous solutions, the dependence on mercury pressure indicated that the heights of both i_1 and $i_1 + i_2$ are strictly linear functions of the square root of the mercury column height. Hence, under such conditions both waves are diffusion controlled. At higher concentrations of hexazinone (Figure 5) the ratio i_1:i_2 changed with mercury pressure indicating deviations from diffusion control.

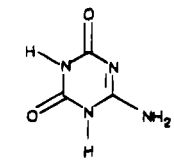
Course of Reduction and Acid–Base Properties of Hexazinone. The pH dependence of the half-wave potentials indicates that for the entire pH range studied, hexazinone is reduced in the protonated form. Therefore, the acid–base properties of hexazinone were investigated.

The compound is reported (*Pesticide Background Statements*, 1985) to be stable for pH 5–9, but our experiments indicated that for pH up to zero the species does not change for the duration of the experiment. Absorption spectra indicate the presence of an acid–base equilibrium. Absorbance at the absorbance maximum of the conjugated base at 244 nm increases with increasing pH (Figure 6) corresponding to an acid–base equilibrium with a pK_a about 1.2. This is in the same pH range as pK_a values for compounds **II** and **III**



pK_a 1.65

(II)



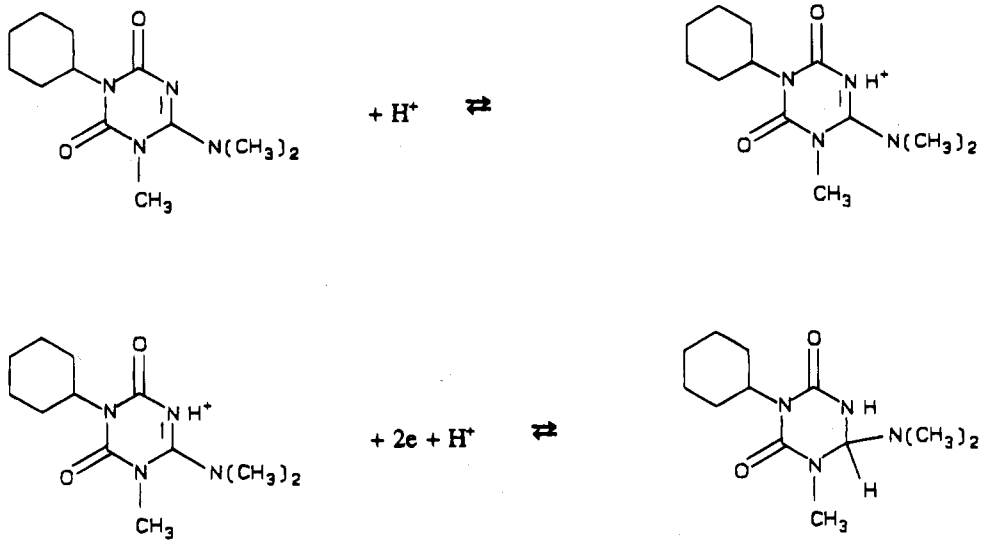
pK_a 1.8

(III)

(Perrin, 1972). Hexazinone cannot undergo tautomeric equilibria, and neither does the model compound **II**. Comparison of pK_a values strongly indicates protonation of the azomethine nitrogen.

The agreement of the intersection of the two linear segments of the $E_{1/2} = f(\text{pH})$ plot (Figure 3) with the spectrophotometrically determined value of pK_a = 1.2 indicates that the same acid–base equilibrium which

Scheme 1



occurs in the bulk of the solution affects the half-wave potentials. For pH <1.2, the protonated form of hexazinone predominates in the solution and the same form is reduced. Therefore, the half-wave potentials in this range are pH-independent. For pH between 1.2 and about 5, the protonated form is reduced but the unprotonated form predominates in the bulk of the solution. Thus, the half-wave potentials are pH-dependent and the magnitude of their shifts with increasing pH indicates the transfer of one proton for each electron transferred.

The dependence of the limiting current i_1 on pH indicates that only the protonated form of hexazinone is reduced. The removal of the protonated form at the electrode surface by reduction perturbs the equilibrium between the protonated and unprotonated forms. The protonated form is generated in the vicinity of the electrode by protonation of the conjugate base. Hence, at pH > pK_a polarographic currents depend both on the concentration of the protonated form in the bulk of the solution and on the rate by which the protonated form is generated. The rate of protonation decreases with increasing pH. When the rate of protonation becomes insufficiently fast, decrease of current i_1 with increasing pH is observed (Figure 2).

Because the protonated form is generated and reduced even at pH values where only a very small fraction of the species is present in the protonated form at equilibrium, the decrease of wave i_1 occurs in a pH range higher than pK_a. The current i_1 has its highest values for pH <2. If the pH where i_1 reaches half of the maximum height is denoted pK', it is possible, using the expression derived by Koutecky (1953), to calculate the rate constant of protonation (k_r)

$$\log k_r = 2\mathrm{p}K' - \mathrm{p}K_a + 0.105 - \log t_1$$

(where t_1 is the drop time). For pK' 4.3, pK_a 1.2, and t_1 = 2.95 s, $\log k_r = 8$ (where k_r is expressed in s^{-1}), which is within the range of rate constants of other protonations.

Hence, both dependences $E_{1/2} = f(\mathrm{pH})$ and $i = f(\mathrm{pH})$ indicate that the reduced species is a protonated form of hexazinone. There is no direct evidence of where the protonation occurs, but there are three circumstantial observations which indicate that the azomethine nitrogen is protonated. First, the pH dependence of the half-wave potentials often indicates that it is the electroactive group which is protonated. Second, the comparison of pK_a values of substituted 1,3,5-triazines, discussed above, indicates preferential protonation of the azomethine nitrogen. Thirdly, the azomethine bond in other compounds is reducible only in the protonated form (Zuman and Exner, 1965; Kubota, 1967; Eisner and Kirowa-Eisner, 1979).

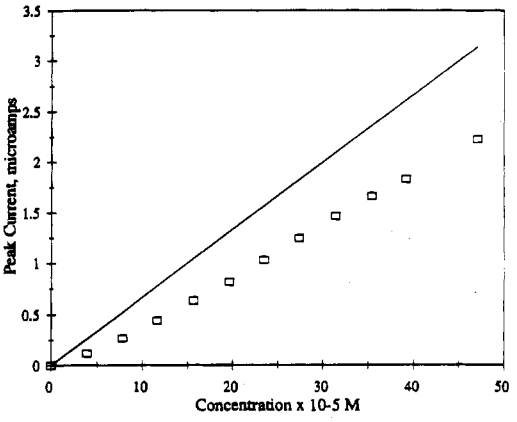


Figure 7. Dependence of DPP peak currents of hexazinone in 0.2 M acetate buffer solutions. (□) 15 mL solutions were shaken for 21 h with 0.3 g of lignin R_1. Solid line is the calibration line which results from a least-squares analysis of peak currents of hexazinone treated similarly but in the absence of lignin.

Thus, the reduction of wave i_1 can be attributed to the sequence shown in Scheme 1. To confirm this reaction path and to enable an interpretation of the process in wave i_2, a comparison of the polarographic behavior of hexazinone with that of related compounds is being carried out and will be reported elsewhere.

Adsorption of Hexazinone on Lignins. Varying volumes of hexazinone stock solution were added to lignin suspensions, and DPP current-voltage curves were recorded after the establishment of equilibrium. The peak currents were plotted as a function of hexazinone concentration and compared with a calibration curve of hexazinone obtained in the absence of lignin (Figure 7). Linear regression was applied to both these curves. From the difference of the two lines—in the absence and presence of lignin—the decrease in concentration of hexazinone due to binding on lignin was obtained. From the known volume of the solution and

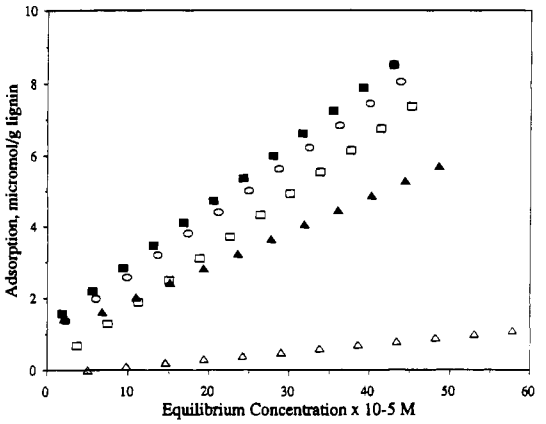


Figure 8. Adsorption of hexazinone on various lignins as a function of the equilibrium concentration. Solutions were 0.2 M acetate buffers of pH 3.7. Shown are the amounts of hexazinone (μmol/g) adsorbed per gram of natural lignin P_1 (■), unwashed natural lignin Q (▲), washed natural lignin Q_1 (△), indulin ATR-CK1 (○), and natural lignin R_1 (□).

Table 1. Desorption of Hexazinone from Aspen Wood Lignin (R_1)[a]

no.	amt adsorbed, μmol/g of lignin	amt desorbed, μmol/g of lignin		amt retained by lignin, %
		first step[b]	second step[b]	
1	8.04	3.21 (39.9%)	1.18 (24%)	45
2	7.72	3.00 (38.9%)	0.98 (21%)	49
3	8.49	3.16 (37.2%)	1.28 (24%)	48

[a] Hexazinone from 3.9×10^{-4} M solution was adsorbed on 0.3 g of aspen wood lignin in 0.2 M acetate buffer, pH 3.7. Desorption into pH 3.7 acetate buffer was measured after shaking for 20–24 h. [b] Each step consisted of treatment of the solid lignin with 15 mL of 0.2 M acetate buffer, pH 3.7.

the known amount of lignin used for the adsorption experiment, the amount of hexazinone adsorbed per gram weight of lignin was computed and plotted as a function of concentration of free, unbound hexazinone, remaining in the solution (Figure 8). Comparison of such Freundlich adsorption isotherms for several lignins indicated that the greatest adsorption capacity is shown by the lignin from maple wood (P_1). The limited solubility of hexazinone in aqueous media prevented an extension of measurements to higher initial concentrations of hexazinone and attaining the saturation regime corresponding to Langmuir isotherms.

The adsorption capacity of the maple wood lignin (P_1) was larger than that of the commercial kraft lignin Indulin ATR-CK1, while the aspen wood lignin (R_1) adsorbed less than the kraft lignin. Lignin from the rotten stump from the Manistee National Forest has shown only a limited adsorption capacity, with the unwashed sample (Q) showing stronger adsorption than the washed sample (Q_1). For this particular lignin prolonged washing resulted in a decrease in adsorption capacity, probably due to changes in its tertiary structure.

Desorption of Hexazinone Bound to Lignin. Desorption studies were carried out with aspen lignin (R_1), chosen because its suspension settled well, which enabled easier decanting of the supernatant fluid. Allowing 20–24 h for the establishment of the desorption equilibrium, a very good reproducibility of the amount of reclaimed pesticide was observed (Table 1). About 47% of the hexazinone remains bound to the lignin after two desorptions, under the conditions used.

When 15 mL of 3.9×10^{-4} M hexazinone was treated with twice the amount of lignin (0.6 g), 4.59 μmol of hexazinone was adsorbed per gram of lignin. In the first step, 2.49 μmol/g was desorbed, indicating that 46% was retained by the lignin.

Table 2. Dependence of the Amount of Hexazinone Desorbed from Lignin on Time[a]

duration of desorption, min	hexazinone adsorbed, μmol/g of lignin	hexazinone desorbed, μmol/g of lignin
20	8.54	3.89 (46%)
40	8.38	3.89 (46%)
60	8.38	3.89 (46%)
80	8.38	3.39 (40%)
100	8.46	3.62 (43%)
1380[b]	8.21	3.89 (47%)

[a] Hexazinone was adsorbed on 0.3 g of aspen wood (lignin R_1) from a 3.9×10^{-4} M solution in 0.2 M acetate buffer, pH 3.7. The desorbed amount was determined by treating the lignin, with the adsorbed hexazinone, with 15 mL of acetate buffer, pH 3.7, for varying periods of time. [b] 23 h.

Table 3. Effect of pH on Desorption of Hexazinone Bound to Aspen Wood Lignin (R_1)[a]

pH	hexazinone	
	amt adsorbed, μmol/g of lignin	amt desorbed, μmol/g of lignin
3.7	9.35	3.13 (33%)
	8.85	2.94 (33%)
4.7	9.45	2.69 (28%)
	9.45	2.69 (28%)
5.7	9.10	
	9.15	1.47–1.71 (16–19%)[b]

[a] Hexazinone was adsorbed on 0.3 g of aspen wood lignin (R_1) from a 3.9×10^{-4} M solution in acetate buffer, pH 3.7. The lignin with the adsorbed hexazinone was shaken for 200 min with 15 mL of acetate buffer of indicated pH. The solid components were separated by centrifugation, and the concentration of hexazinone in the supernatant was determined after adjusting the pH to 3.7. [b] Considerable uncertainty due to elution of lignin components that catalyze evolution of hydrogen at the DME and limit the accuracy of the measured peak current; this elution was accompanied by a darker color of the eluate.

The dependence of desorption on time was followed by exposing hexazinone (bound to solid lignin) to pH 3.7 acetate buffer for various periods of time (Table 2). On the average, about 56% of the hexazinone remained retained by the lignin. The establishment of the desorption equilibrium is rapid, the desorption is practically complete in 20 min.

To investigate the role of pH on desorption, lignin with known amounts of bound hexazinone was exposed to acetate buffers of pH varying between 3.7 and 5.7. After the desorption equilibrium was established, the pH of the solution was adjusted to 3.7 and the amount of released hexazinone determined (Table 3). The desorbed amount decreases with increasing pH and hence the higher the pH (within the studied range) the more hexazinone remains bound to the lignin.

Comparison of the values for desorption after one cycle in Table 1 (average 38.7%), Table 2 (average 44.7%), and Table 3 (at pH 3.7 average 33%) shows variations due to nonhomogeneity of lignin samples as well as limited reproducibility of the adsorption–desorption procedure.

Conclusions. Compared to other pesticides used frequently by the Forest Service, and studied earlier, such as acifluorfen, thiram, and DCNA (Rupp and Zuman, 1992), hexazinone is much less strongly adsorbed on solid lignin particles. The desorption is very fast and seems to be little dependent on pH in the range (pH 3.7–5.7) studied. Similarly as for the above-mentioned pesticides, part of the hexazinone (at least

40%) is bound irreversibly and hence remains bio-unavailable. The fast desorption indicates that most of the bioavailable 60% is active practically immediately.

Polarographic waves of hexazinone at pH 3.7 were found suitable for determination of hexazinone, in the presence of solid particles of lignin. The reduction occurs at much more negative potentials than for the pesticides studied earlier (Rupp and Zuman, 1992). Lignin preparations invariably contain smaller fragments which are water soluble. Some of these low molecular weight fragments are reduced in the potential range where hexazinone is reduced. Moveover, they also catalyze hydrogen evolution and the resulting current interferes with the hexazinone waves. Thus, in this case, dc polarography was replaced by DPP. The accuracy of the measured peak currents in DPP are, nevertheless, more affected by the presence of soluble surface active fragments of lignin than dc polarographic currents. Consequently, the analytical results obtained with DPP, on which the adsorption data are based, are less reliable than when dc polarography can be used. The application of DPP to the studies of the adsorption of hexazinone is facilitated by the fact that the reduction of hexazinone occurs at relatively negative potentials, where the adsorption of surfactants from lignin is less important.

ACKNOWLEDGMENT

This project has been supported by the Department of Agriculture, Forestry Service, Grant 42-710.

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Received for review September 19, 1994. Accepted September 22, 1994.[⊗]

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1994.