Oxidative Degradation of Ethylenethiourea (ETU) and ETU Progenitors by Hydrogen Peroxide and Hypochlorite

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The mechanism of hydrogen peroxide and hypochlorite mediated oxidations of ethylenethiourea (ETU) was reinvestigated. Evidence is presented which suggests that, in water, a radical dissociation of the intermediate 2-imidazolin-2-yl sulfinate (ETU-O_2) and subsequent trapping by solvent results in 2-imidazoline hydrosulfite which is, in turn, rapidly oxidized to 2-imidazoline hydrosulfate. Alternately, ETU-O_2 may be oxidized to 2-imidazolin-2-yl sulfonate (ETU-O_3) in low yield. In 1% bicarbonate solution ethyleneurea (EU) is the major product of ETU oxidation whether hypochlorite or hydrogen peroxide is used as the oxidant. A mechanism for the oxidations of ETU that is consistent with radiotracer and spectroscopic studies is proposed. Although ethylenebis(dithiocarbamate) (EBDC) formulations are degraded by hydrogen peroxide, this oxidant is less effective than hypochlorite due to oxidant destruction by metal cations in the formulation. Whereas Jaffe's base [1-(2′-imidazolin-2′-yl)-2-imidazoïidinethione], which is a potential source of ETU, is rapidly inactivated by hypochlorite, it reacts only slowly with aqueous hydrogen peroxide to form the corresponding sulfenate.

A recent report (Marshall, 1978) of the facile oxidation of ethylenebis(dithiocarbamate) (EBDC) fungicides by alkaline hypochlorite suggests that the conversion of residues of these fungicides (present on the surface of treated agricultural produce) to the oncogen ethylenethiourea (ETU, I) during normal industrial processing may be avoided. ETU is oxidized to ethyleneurea (EU, II) and sulfate (Marshall and Singh, 1977), while EBDC fungicides (Maneb, Zineb, and Mancozeb) and ethylenethiuram monosulfide (ETM), a field degradation product of EBDCs, are also rapidly oxidized, thus preventing their subsequent decomposition to ETU (Marshall, 1978). A preprocessing wash with dilute alkaline hypochlorite of the field-treated agricultural produce followed by a second wash containing bisulfite has been suggested as a means of eliminating these toxic chemicals.

2-Imidazoline has been identified as a product of EBDC and ETU metabolism in animals (Iverson et al., 1977), plants (Vonk, 1975, 1976), and soils (Kaufman and Fletcher, 1973) and of the nonbiological oxidation of ETU (Vonk, 1975b). However, the relationship of 2-imidazoline to EU, the other major decomposition product, remains unclear. Further, the identification of *N*-formylethylenediamine and ethylenediamine (EDA) (along with EU) as metabolites of EBCDs in leafy plants (sugar beets, lettuces, or turnips; Lyman, 1971) seems inconsistent with an oxidative degradation involving EU. During a search for other potential oxidants of EBDCs we had occasion to reinvestigate the action of hydrogen peroxide on these substrates. The work reported here elaborates on mechanistic pathways for the oxidation of ETU and confirms previous findings.

EXPERIMENTAL SECTION

Materials. Ethylenethiourea (ETU, I, [2-imidazolidinethione) and ethyleneurea (EU, III, [2-imidazolidineone) were purchased from Fisher Scientific Co. ETU was recrystallized from methanol/water (1:1) containing 5% hexane and EU was sublimed at 105 °C (10^{-3} mm) and recrystallized from methanol prior to use.

ETU dioxide (2-imidazolin-2-yl sulfinate, III) and ETU trioxide (2-imidazolinyl-2-yl sulfonate, IV) were prepared according to previously published procedures (Marshall and Singh, 1977). 2-Imidazoline was prepared by reaction of ethylenediamine with 1.2 equiv of hydrogen cyanide according to the method Jentzsch and Seefelder (1965) or by the action of *tert*-butyl isocyanide on ethylenediamine (Ito et al., 1973). The highly hydroscopic product was induced to crystallize only upon high vacuum sublimation of the distilled product. Dropwise addition of 1 equiv of concentrated sulfuric acid to an ethanolic solution of 2-imidazoline resulted in immediate formation of a precipitate (V), which was isolated by filtration and washed liberally with anhydrous ethanol.

N-Formylethylenediamine (VI) was obtained by hydrolysis of 2-imidazoline. Conversion to the hydrochloride salt and recrystallization from methanol water furnished an analytical sample: mp 106 °C; NMR δ 2.75 (t, 2 H, $J_{NCH_2CH_2}$ = 6 H_z), 3.33 (t, 2 H, $J_{NCH_2CH_2}$ = 6 H_z), 8.13 (s, 1 H).

2,2′-Bis(2-imidazoline) was prepared by reaction of ethyl bromide with dithioxamide in ethanol according to the method of Wang and Bauman (1965). The crude product, *N*,*N*′-diethyl-1,2-dithioethylenediamine dihydrobromide, was treated with ethylenediamine to give the desired bisimidazoline in 80% yield. The dihydrosulfate salt (VII) was prepared by dropwise addition of concentrated sulfuric acid to an ethanolic solution of the bisimidazoline. The resulting precipitate was isolated by filtration and liberally washed with ethanol. Recrystallization from water afforded white crystals: mp 280–281 °C; NMR δ 3.69 (*N*-methylene, s).

Jaffe's base [1-(2′-imidazolin-2-yl)-2 imidazolidinethione, VIII] was conveniently prepared by the dropwise addition of 1 equiv of *N*-chlorosuccinimide slurried in ethanol, to an ice-cold stirred solution of ETU in ethanol. When addition was complete, the crude reaction mixture was stirred for a further 30 min and then the precipitated product was isolated by filtration. The corresponding free base was obtained by passing the crude product through a weakly basic ion-exchange column using methanol/water (1:1) as eluant. Recrystallization from ethanol raised the melting point from 219 to 235 °C (mp 236–238 °C; Poos et al., 1959).

Thin-Layer Chromatography (TLC). Compounds were spotted on silica gel plates (0.25 mm, Polygram-Macherey Nagel & Co.) containing fluorescent indicator or on cellulose plates (0.25 mm, Camag Co.) and developed in methanol, methanol/acetic acid (9:1), or chloro-

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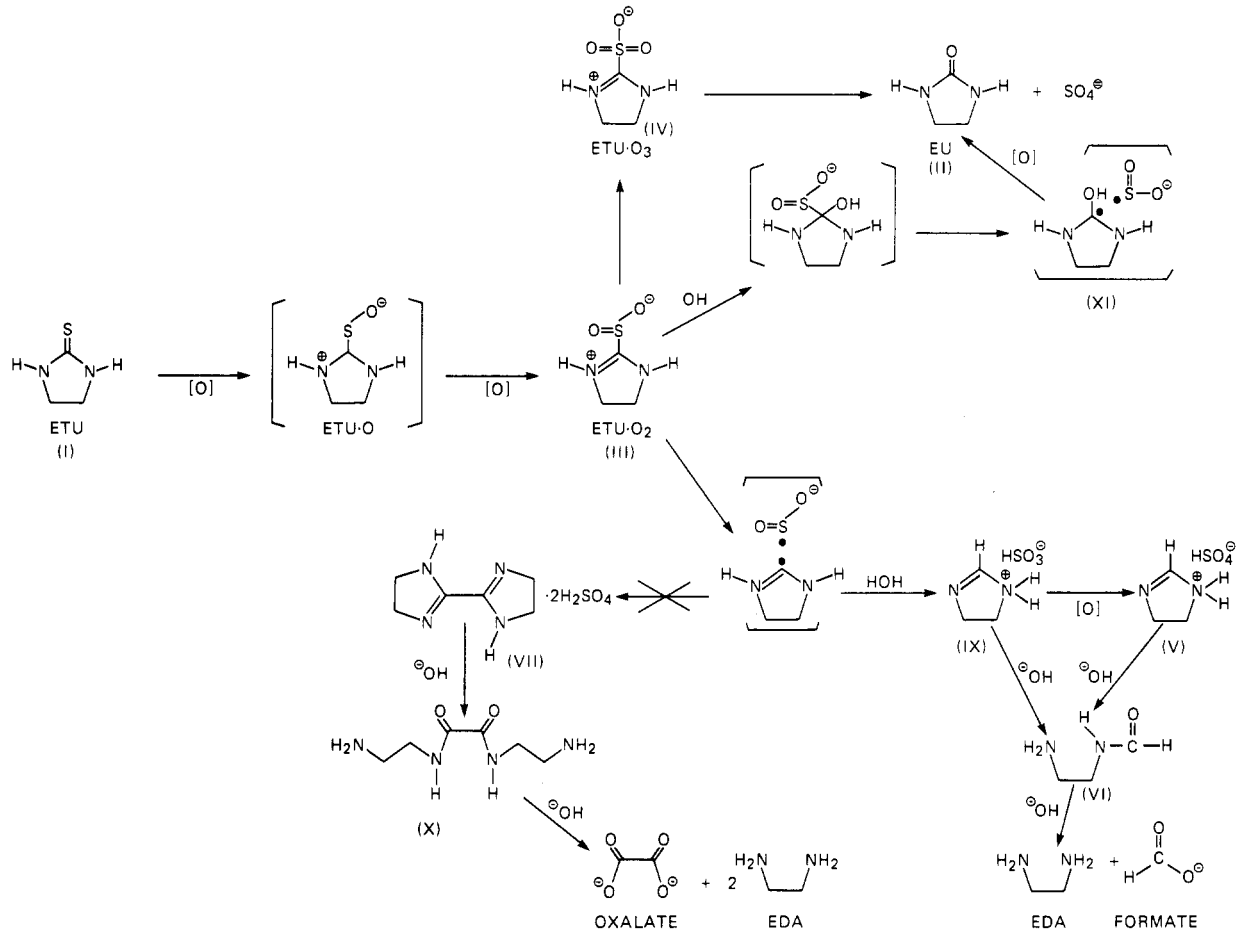

Figure 1. Oxidative decomposition of ETU and subsequent hydrolysis of the products.

form/methanol (5:1) (silica gel) or in isopropyl alcohol/water (3:7) (cellulose). Spots were visualized using Grote's reagent (Grote, 1931), ferricyanide–nitroprusside, or *N*,*N*′-dimethylaminocinnamaldehyde in 3:1 ethanol/4 N hydrochloric acid. When chromatographically pure 4,5-[^{14}C]ETU was used as a substrate for oxidation, the products (separated by TLC) were quantified by scintillation counting with appropriate corrections for background and quenching.

Equipment. IR spectra were recorded as KBr pellets using a Beckman IR-20A spectrophotometer. EPR spectra were recorded at room temperature in D_2O on a Varian 3 EPR spectrometer. The MS were determined on a Finnigan 3100 MS coupled to a D 6000 data acquisition system. Samples were determined by direct inlet probe. Proton NMR spectra were recorded in D_2O on a Varian T-60 NMR spectrometer.

RESULTS AND DISCUSSION

Previously it was reported that the oxidation of ethylenethiourea (ETU, I) with excess hydrogen peroxide resulted in the consumption of 3 equiv of this oxidant per equivalent of substrate. The final product was considered to be 2-imidazoline sulfonate (ETU-O_3, IV) and 2-imidazoline sulfinate (ETU-O_2, III) demonstrated to be an intermediate (Marshall and Singh, 1977). Intermediate III was decomposed by strong base (3 M ammonium hydroxide), resulting in the formation of dithionite (hydrosulfite) via a SO_2 ion radical. The fate of the other fragment (presumably 2-imidazolinyl radical) was not further investigated. Experiments that define the products of this decomposition and are in agreement with the results of Vonk (1975a,b) are now reported.

When ETU-O_2 (III) was dissolved in D_2O and monitored by proton NMR it was rapidly degraded to a new product, IX (Figure 1), as evidenced by an upfield shift of the *N*-methylene proton singlet (from δ 4.08 to 4.01). Moreover, when the rearrangement was conducted in water, the product IX was observed to have a downfield singlet (account for one proton) at δ 8.23 in addition to the singlet at 4.01 (four protons). Oxidation of the rearranged material with hydrogen peroxide resulted in the consumption of 1 equiv of oxidant. The oxidized product had an NMR spectrum identical with the rearranged product in water IX and was characterized as 2-imidazoline hydrosulfate (V).

Thus, oxidation of ETU in aqueous solution with excess hydrogen peroxide consumes 3 equiv of oxidant and results in the formation of 2-imidazolinyl sulfonate (IV) and/or 2-imidazoline hydrosulfate (V).

The estimated half-life of ETU-O_2 (III) in D_2O (NMR, at room temperature), where no special precautions were taken to exclude air, was 22 min. This decomposition, when monitored by EPR (D_2O, room temperature, closed liquid cell), was accompanied by the formation of paramagnetic species. The unsplit signal was identical with and accounted for over 25% of the signal derived from 1 equiv of sodium dithionite. The stability of this species was a function of the degree to which air was excluded from the system. When monitored by UV, a transient absorption was observed at 313 nm and here, as well, the strength and stability of the absorbance were a function of the efficiency with which air was excluded from the reaction system. Sodium dithionite (hydrosulfite) in the same solvent system behaved similarly.

A reaction pathway which accounts for these products

Table I. Variation in the Product Distribution Resulting from Oxidation of 4,5-[^{14}C]ETU by Hypochlorite or by Hydrogen Peroxide in 1% Sodium Dicarbonate or in Water

oxidant	solvent	run no.	products			origin	% of total activity applied
			ETU	EU	ETU-O_3		
NaOCl	1% bicarbonate	1	12.5	53.8	ND[a]	32.2	98.5
		2	2.5	79.0	ND	19.0	100.5
		3	6.7	75.1	ND	12.8	94.6
		4		89.2	ND	14.5	103.7
		5	3.1	94.6	ND	3.9	101.6
		$\bar{x}$(1→5)	5.0 ± 4.7	78.3 ± 16.1		16.5 ± 10.4	
		$\bar{x}$(2→5)	3.1 ± 0.8	84.5 ± 9.0		12.6 ± 6.4	
H_2O_2	HOH	6	3.6	4.3	7.3	78.6	93.8
		7	2.3	4.5	10.5	76.3	93.6
		8	2.1	1.6	11.4	73.4	93.5
		$\bar{x}$(6→8)	2.7 ± 0.8	3.5 ± 1.6	9.7 ± 2.2	76.1 ± 2.6	
H_2O_2	1% bicarbonate	9	3.3	90.6	4.5	2.7	101.1
		10	0.7	80.4	5.8	13.2	100.1
		11	0.5	82.2	7.1	10.3	100.1
		$\bar{x}$(9→11)	1.6	84.4 ± 7.7	5.8 ± 1.3	8.7 ± 5.4	

[a] ND, none detected.

is diagrammed in Figure 1. A homolytic cleavage of the C–S bond in ETU-O_2 (III) results in an intimate radical ion pair, which is rapidly trapped by water resulting in 2-imidazoline hydrosulfite (IX). Hydrosulfite IX is, in turn, rapidly oxidized to the hydrosulfate V. A competing oxidation of ETU-O_2 results in formation of ETU-O_3 (IV). Efforts to interconvert these two products, IV and V by the action of base, heating, or hypochlorite were unsuccessful. Sulfonate IV is converted to EU (II) slowly by the action of base or rapidly by oxidation with sulfite or hypochlorite.

Decomposition of the radical ion pair might result in biimidazoline (or its dihydrosulfate salt VII) via a dimerization of the 2-imidazolinyl radical. The free base of VII is only moderately stable in D_2O and decomposes to *N,N'*-bis(2-aminoethyl)oxamide (X) (Wang and Bauman, 1965) or in stronger base to oxalate and ethylenediamine (Woodburn and O'Gee, 1952). The dihydrosulfate salt VII is quite stable in D_2O. The estimated half-life of the corresponding free base was found to be 120 min. No evidence could be found (by TLC or NMR) for the formation of VII or its free base in any of the decomposition studies even under conditions in which the intermediate dithionite was quite stable and persisted for at least 1 h.

A further study of the competing oxidation vs. radical dissociation of ETU-O_2 demonstrated that the latter reaction is temperature dependent. An aqueous solution of this substrate when oxidized with excess H_2O_2 in an ice bath for 2 h gave ETU-O_3 (IV) if the crude reaction mixture was freeze-dried, but resulted only in 2-imidazoline hydrosulfate (V) if solvent and excess oxidant were removed on a rotary evaporator. Moreover, the yields of product were nearly quantitative (>95%).

The effect of added base upon the course of peroxide oxidation was demonstrated by comparing product yields from labeled ETU in water and 1% bicarbonate. ETU in 1% bicarbonate or in water was doped with active carrier and treated with a slight excess of oxidant and allowed to react at room temperature for 20 min in the dark. A suitable aliquot of the reaction mixture was spotted on a TLC plate and eluted to separate the various products. The individual components were then quantified by scintillation counting. Results are reported in Table I. In water, 76% of the activity remained at the origin and 3.5% corresponded to EU, whereas in 1% bicarbonate, (pH 8.8), EU accounted for 85% of the activity and material remaining at the origin accounted for 9% of the total activity. In both cases ETU-O_3 was a minor product. In the case of 1% bicarbonate the product distribution from oxidation with hydrogen peroxide closely paralleled the product distribution from hypochlorite oxidation in the same medium. The identity of the material at the origin from oxidation in water was demonstrated to be 2-imidazoline hydrosulfate by cochromatography (on cellulose plate) with authentic standard.

The variability in product yields from oxidations under the same experimental conditions reflects the radical nature of the oxidation mechanism. Because ETU-O_3 in 1% bicarbonate remains essentially unaffected by hydrogen peroxide (less than 0.1 equiv of oxidant consumed per equivalent of substrate; Table II), and alternate route to EU is therefore necessary. A mechanism which is consistent with experimental results is included in Figure 1. Hydroxide attack upon ETU-O_2 (III) and subsequent radical scission of the C–S bond (homolytic cleavage) results in an intimate radical ion pair XI which is trapped by solvent and oxidized to EU and sulfate. An analogous reaction mechanism has been used to explain the reduction of Cd^{2+} to cadmium metal by thiourea dioxide (which is oxidized to urea) (McGill and Lindstrom, 1977). Thus, for ETU oxidation, the concentration of base determines the relative yields of 2-imidazoline hydrosulfate (V) and ethylene urea (II).

Although hydrosulfate V is stable in neutral solution, the corresponding free base is rapidly hydrolized to *N*-formylethylenediamine (VI) and more slowly to formate and ethylenediamine by the action of acid or base. In D_2O, 2-imidazoline had an estimated half-life of 4.5 min, and in buffered solution (potassium dihydrogen phosphate–sodium phosphate, 1:1, pH ~6.7, or sodium acetate–acetic acid, 1:1, pH ~5.8) this value was increased only slightly to 6.5 and 8.0 min, respectively. The consumption of hypochlorite by 2-imidazoline hydrochloride, by ethylenediamine dihydrochloride, and by biimidazoline dihydrosulfate in 1% sodium bicarbonate or in 1 N sodium hydroxide is reported in Table II. The observation that each substrate consumes several equivalents of oxidant precludes their intermediacy on the oxidative pathway between ETU and EU, nor can they be major oxidation byproducts. Earlier studies (Marshall, 1977) have demonstrated the consumption of only 4 equiv in this transformation. These results are not surprising in that

Table II. Variation of the Consumption of Oxidant (Hydrogen Peroxide or Hypochlorite) with Time by Jaffe's Base, 2-Imidazoline, Ethylenediamine, Biimidazoline, and 2-Imidazolin-2-yl Sulfonate

substrate	oxidation conditions[a] oxidant	water	1% bicarbonate	1 N sodium hydroxide	time, min
Jaffe's base-HCl (VIII)	H_2O_2	0.25	2.28		15
			3.11		30
		0.40			40
			3.37		45
			3.48		60
		0.77	3.85		90
			4.17		110
			4.51		160
		0.95			180
	NaOCl		4.31	6.45	10
			4.90	9.10	30
				9.90	45
			5.82	9.95	60
			6.243		110
				10.7	120
			6.50		140
			6.60		180
2-imidazoline hydrochloride	NaOCl		0.72	3.46	10
				4.75	30
			4.12		60
				5.38	120
			6.95		150
EDA·2HCl	NaOCl		1.03	7.15	10
			2.13		20
				7.24	30
			3.39		40
				7.30	60
			5.23		70
			5.54		120
biimidazoline dihydrosulfate (VII)			0.76	0.90	10
				0.90	20
			2.11		30
			5.83		80
2-imidazolin-2-yl sulfonate (ETU-O_3, IV)			0.05		10
			0.11		20
			0.08		30

[a] Results are expressed as equivalents of oxidant consumed (per equivalent of substrate) after time T (min).

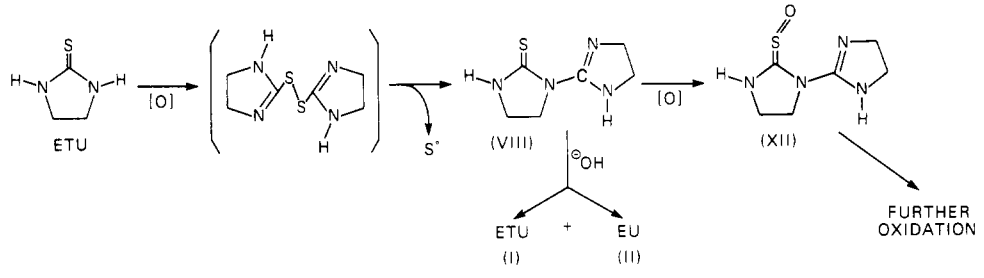

Figure 2. Formation and degradation of Jaffe's base (VIII).

amines (Bachmann et al., 1954; Haberfield and Pau, 1965), ammonia (Weil and Morris, 1949), and ammonium ions are known to react rapidly with hypochlorite forming reactive *N*-chloroamines which in turn suffer further degradation.

The efficiency with which hydrogen peroxide will oxidize EBDC fungicides so as to prevent their subsequent decomposition to ETU was measured in the following experiments. Formulated Maneb (slurried in 1% sodium bicarbonate or in N sodium hydroxide) was oxidized with a large excess of H_2O_2 at room temperature for 20 min and then an excess of sulfite (to remove unreacted oxidant) was added. The reaction flasks were then gently boiled for 2 h to ensure conversion of EBDC residues to ETU. This treatment was found to reduce the yield of ETU 86.5% (1 N sodium hydroxide) and 87% (1% bicarbonate) relative to controls in which no oxidant was added, whereas addition of sodium sulfite alone did not affect the yield of ETU. However, the yield of ETU (from Maneb in 1% bicarbonate) was only reduced 14% relative to controls when only 24 equiv of H_2O_2 was used (a similar quantity of hypochlorite reduced ETU formation 100%). Divalent cations are known to accelerate the decomposition of hydrogen peroxide to hydroxide and hydroxyl radicals (Shanley and Greenspan, 1947; Schumb, 1949). The products of hydrogen peroxide decomposition will not oxidize iodide, precluding iodometric determinations of the quantity of oxidant which remained. Furthermore, the products are ineffective in inactivating Maneb under the conditions used. Because manganous sulfate will rapidly consume more than 16 equiv of H_2O_2 in 10 min and manganese salts are an integral part of the Maneb formulation, this oxidant is considered to be less effective than hypochlorite for EBDC oxidations to prevent sub-

sequent decomposition to ETU.

Fate of Jaffe's Base on Oxidation. Jaffe's base (1,2′-imidazolinyl)-2-imidazolidinethione VIII) has been demonstrated to be a product of ETU decomposition in soils (Kaufman and Fletcher, 1973), in plants (Lyman, 1971; Rhodes, 1977), and of ETU oxidation, both photolytic (Cruickshank and Jarrow, 1973) and chemical (Johnson and Edens, 1941). As this compound is a potential source of ETU (as suggested in Figure 2), its stability to acid and base hydrolysis was investigated. At room temperature this substrate was unchanged by 1% bicarbonate, 1 N sodium hydroxide, or 0.5 M phosphate buffer (adjusted to pH 4). At elevated temperature this product was slowly hydrolyzed to ETU and EU in basic solution only and remained unchanged in the phosphate buffer. The estimated half-life of this substrate at 100 °C in 1% bicarbonate and in 1 N sodium hydroxide was 46 and 18 min, respectively.

Jaffe's base is susceptible to both hypochlorite and hydrogen peroxide oxidation. Substrate VIII (as the hydrochloride salt) was observed to consume slowly 1 equiv of hydrogen peroxide (Table II) in water. The product, a colorless oil which could not be induced to crystallize is tentatively assigned the structure [XII 1-(2-imidazolin-2-yl)-2-imidazoline sulfenate] as the hydrochloride salt. The assignment is based on spectroscopic properties [NMR δ 3.8 (s, 4 H), 3.62 (t, 2 H), 3.35 (t, 2 H); IR 870 cm^{-1}; (trisubstituted thiourea monoxide; Walter and Randau, 1969)], positive chemical tests with ferric chloride and Grote's reagent, and the expected stability of sulfenates resulting from trisubstituted thioureas (Walter and Randau, 1969). This assignment was corroborated by elemental analysis. Anal. Calcd for $C_6H_{10}N_4SO \cdot HCl \cdot 2HOH$: C, 27.96; H, 5.87; N, 21.74; S, 12.44; Cl, 13.37. Found: C, 28.16; H, 6.07; N, 21.64; S, 12.68; Cl, 13.93. As demonstrated in Table II, substrate VIII consumed hydrogen peroxide more rapidly in 1% bicarbonate than in water and the rate of oxidation was further increased by using hypochlorite as oxidant. Although these reactions were not investigated in detail, inactivation studies (using procedures described above) using an excess of hypochlorite (10 equiv) demonstrated that the formation of ETU from base hydrolysis could be eliminated (reduced by 100%) by hypochlorite oxidation in 1% bicarbonate or in 1 N sodium hydroxide. The same results were observed when only 5 equiv of oxidant (in either solvent system) were used. Thus, it is suggested that the rate of attack by oxidant on the thiocarbonyl group of VIII is at least competitive with the rate of attack on the imidazoline ring nitrogen.

In summary, hydrogen peroxide oxidation of ETU leads (via ETU-O_2) to 2-imidazoline hydrosulfate (V) and/or ethyleneurea (II), with 2-imidazoline sulfonate (IV) as a minor product. Base hydrolysis of the former results in ethylenediamine via *N*-formylethylenediamine. These hydrolysis products have been identified as metabolites of Mancozeb (mixed manganese, zinc EBDC) in rats (Lyman, 1971).

Jaffe's base (VIII) may be hydrolyzed by base to ETU and EU. However, if present as a surface contaminant on field treated produce, the capacity of this product to degrade (on subsequent industrial processing) to ETU may be eliminated by pretreating the produce with an alkaline oxidative wash.

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