

Oxidation by Metal Salts. X. One-Step Synthesis of γ -Lactones from Olefins

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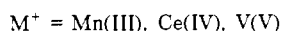
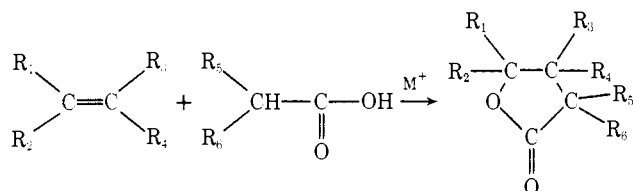
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Abstract: This paper describes a novel one-step synthesis of γ -lactones by the reaction of manganic and other higher valent metal carboxylates with readily available olefins and carboxylic acids. A free radical mechanism involving the selective generation and oxidation of organic free radicals is presented.

As part of our studies on the oxidation mechanisms of metal carboxylates, we have observed¹ a novel reaction of manganic and ceric carboxylates with olefins leading to γ -butyrolactones in excellent yields. This paper is intended to summarize our work on the development of this simple one-step synthesis of γ -lactones from olefins and to establish the free radical mechanism for formation of these lactones.

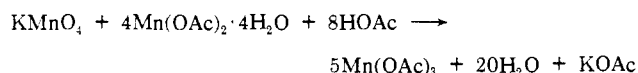
Results

Lactone Synthesis. The lactone synthesis involves the preparation of γ -butyrolactones from readily available olefins and carboxylic acids in a simple one-step process. The general reaction which is depicted below consists of the addition of a carboxylic acid having an α -hydrogen atom across the double bond of an olefin in the presence of stoichiometric amounts (2 equiv/mol of lactone) of various metal oxidants. Higher valent metal salts of manganese, cerium, and vanadium have been used successfully in the



lactone synthesis. Most of our studies, however, have utilized manganese compounds because of their ready availability and high solubility.

Synthetic Procedure for the Preparation of Lactones. Manganic acetate dihydrate was used to synthesize the lactones shown in Table I. However, the most convenient laboratory preparation of γ -lactones involved the *in situ* formation of manganic acetate by the reaction of potassium permanganate on manganous acetate.



This procedure permits the one-step preparation of γ -lactones from such readily available reagents as KMnO_4 , $\text{Mn}(\text{OAc})_2$, an olefin, and a carboxylic acid.

Nature of the Olefin. Examples of γ -butyrolactones formed from a variety of olefins are shown in Table I. The yields of lactone obtained were based on the metal oxidant used, and no attempt was made to maximize the yield for each olefin. Yields based on olefin consumed were generally higher, as evidenced by the relative absence of significant side products. High yields of lactones were obtained from both internal and terminal olefins, although the terminal olefins appeared approximately five times more reactive

under competitive conditions (Table III). In all cases examined, the structure of the lactones obtained from terminal olefins was as shown in Table I, with the oxygen of the carboxylic acid bonded to the more substituted 2 position of the olefin.

Isomeric internal olefins such as *cis*- and *trans*-octene-4 gave similar mixtures of isomeric lactones in a 5:1 ratio, whereas cyclooctene and *trans*-stilbene produced only one lactone isomer each. A single, presumably *trans*, lactone was obtained from both *cis*- and *trans*- β -methylstyrene. In all these reactions, no significant isomerization of the unreacted olefins was observed during the course of the reaction.

Lactones have also been obtained from dienes, both non-conjugated, such as hexadiene-1,5 and octadiene-1,7 and conjugated diolefins, such as butadiene and isoprene. In the case of isoprene, addition occurred at both double bonds, but the predominant product with both acetic acid and cyanoacetic acid involved addition to the more substituted olefinic bond.

Preference for terminal attack in polyunsaturated olefins was suggested by the high yield of lactone obtained from 4-decyn-1-ene; the hydrogenated form of this lactone was reported to be a mammalian pheromone isolated from the male tarsal organ in black-tailed deer.³

Nature of the Carboxylic Acid. While acetic acid was used most frequently in the lactone synthesis, other acids have also been successfully utilized for the preparation of γ -lactones having the appropriate substituents in the α position. Thus, propionic acid gave high yields of α -methyl butyrolactones, cyanoacetic acid readily formed α -cyano lactones, isobutyric acid gave α -*gem*-dimethyl butyrolactones (albeit in low yields), and succinic acid led to α -carboxymethylene butyrolactones. These experiments indicate the generality of the lactone synthesis and suggest the possibility of preparation of a large variety of α -substituted γ -butyrolactones by the proper choice of the carboxylic acid component.

Nature of the Metal Oxidant. Higher valent metal salts of manganese, cerium, and vanadium have been used successfully in the lactone synthesis. Of the metal ions, the salts of manganese have been most extensively used due to their ready availability and high solubility. The manganese reagent most frequently used was manganic acetate dihydrate, $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$, which was readily prepared by permanganate oxidation of manganous acetate² and could be stored for extended periods of time. Other manganic salts used in the lactone synthesis include anhydrous manganic acetate made from manganous nitrate and acetic anhydride, activated MnO_2 freshly prepared, and now available commercially, and Mn_2O_3 formed by air oxidation of manganous ion in basic solution. For preparative purposes, it was found convenient to use manganic acetate generated

Table I. Lactones Obtained from the Reaction of Manganic Acetate with Olefins

Olefin	Acid	Lactone ^a	Yield, % ^b
C ₆ H ₁₃ CH=CH ₂	CH ₃ COOH	R ₁ = C ₆ H ₁₃	74
C ₆ H ₅ CH=CH ₂	CH ₃ COOH	R ₁ = C ₆ H ₅	60
C ₆ H ₅ C(CH ₃)=CH ₂	CH ₃ COOH	R ₁ = C ₆ H ₅ ; R ₂ = CH ₃	74
(CH ₃) ₂ C=CH ₂	CH ₃ COOH	R ₁ , R ₂ = CH ₃	30
(CH ₃) ₃ CCH=CH ₂	CH ₃ COOH	R ₁ = (CH ₃) ₃ C	48
C ₃ H ₇ CH=CHC ₃ H ₇ (trans)	CH ₃ COOH	R ₁ , R ₄ = C ₃ H ₇ ^c	44
C ₆ H ₅ CH=CHC ₆ H ₅ (trans)	CH ₃ COOH	R ₁ , R ₄ = C ₆ H ₅ ^d	16
C ₆ H ₅ CH=CHCH ₃ (trans)	CH ₃ COOH	R ₁ = C ₆ H ₅ ; R ₄ = CH ₃ ^d	79
Cyclooctene		R ₁ , R ₃ = -(CH ₂) ₆ -	62
C ₆ H ₅ CH=CHCOOCH ₃	CH ₃ COOH	R ₁ = C ₆ H ₅ ; R ₄ = COOCH ₃	45
Hexadiene-1,5	CH ₃ COOH	R ₁ = CH ₂ =CH(CH ₂) ₂ -	24
Octadiene-1,7	CH ₃ COOH	R ₁ = CH ₂ =CH(CH ₂) ₄ -	26
Butadiene	CH ₃ COOH	R ₁ = CH ₂ =CH-	30
Isoprene	CH ₃ COOH	R ₁ = CH ₂ =C(CH ₃)- + (R ₁ = CH ₂ =CH-; R ₂ = CH ₃)	13 + 37
CH ₃ (CH ₂) ₄ C≡CCH ₂ CH=CH ₂	CH ₃ COOH	R ₁ = CH ₃ (CH ₂) ₄ C≡CCH ₂	50
C ₆ H ₅ CH=CH ₂	CH ₃ CH ₂ COOH	R ₁ = C ₆ H ₅ ; R ₅ = CH ₃	50
C ₆ H ₅ CH=CH ₂	CNCH ₂ COOH	R ₁ = C ₆ H ₅ ; R ₅ = CN	41
C ₆ H ₁₃ CH=CH ₂	CNCH ₂ COOH	R ₁ = C ₆ H ₁₃ ; R ₅ = CN	60
C ₆ H ₅ C(CH ₃)=CH ₂	CNCH ₂ COOH	R ₁ = C ₆ H ₅ ; R ₂ = CH ₃ ; R ₅ = CN	43
Octene-4	CNCH ₂ COOH	R ₁ , R ₄ = C ₃ H ₇ ; R ₅ = CN	49
C ₆ H ₅ CH=CHCH ₃	CNCH ₂ COOH	R ₁ = C ₆ H ₅ ; R ₄ = CH ₃ ; R ₅ = CN	51
Isoprene	CNCH ₂ COOH	(R ₁ = CH ₂ =C(CH ₃)-; R ₅ = CN) + (R ₁ = CH ₂ =CH-; R ₂ = CH ₃ ; R ₅ = CN)	5 + 39
C ₆ H ₁₃ CH=CH ₂	CH ₂ COOH	R ₁ = C ₆ H ₁₃ ; R ₅ = CH ₂ COOH	25
	CH ₂ COOH		

^a Where not specified R's = H. ^b Yield based on manganic acetate dihydrate used. ^c Two isomers in the ratio 5:1 were obtained. ^d Only one isomer (presumably trans) was obtained.

Table II. Lactone Yields Obtained with Various Metal Oxidants

Oxidant	Olefin	Acid	Lactone yield, % ^a
Mn(OAc) ₃ ·2H ₂ O	Octene-1	HOAc	74
Mn(OAc) ₃ (anhydrous)	Octene-1	HOAc	65
MnO ₂ (activated)	Octene-1	HOAc	46-67
Mn ₂ O ₃	Octene-1	HOAc	61
Mn(OAc) ₃ (<i>in situ</i>)	Decene-1	HOAc	67
Ce(OAc) ₄	Styrene	HOAc	70
Ce(NH ₄) ₂ (NO ₃) ₆	Octene-1	HOAc	48
NH ₄ VO ₃	α-Methylstyrene	HOAc	67

^a Vpc yield based on oxidant used, assuming 2 equiv of oxidant per mole of lactone.

in situ from potassium permanganate and manganous acetate tetrahydrate or dihydrate. Under all these conditions, lactone yields of 60-70% based on oxidant used were obtained from terminal olefins.

The ceric(IV) salts used in the lactone synthesis included ceric acetate, Ce(OAc)₄, prepared by ozonolysis of cerous acetate,⁴ and the commercially available ceric ammonium nitrate, Ce(NH₄)₂(NO₃)₆, in the presence of potassium acetate.

The vanadium(V) salt used in the lactone synthesis was ammonium metavanadate, NH₄VO₃, in the presence of added potassium acetate and acetic anhydride.

A summary of the lactone yields obtained with the various metal oxidants is shown in Table II.

Effect of Reaction Variables. The lactone synthesis is generally conducted in the temperature range of 120-180° either in a refluxing system or in sealed tubes. Increasing the reaction temperature dramatically decreased the reac-

tion time, from several hours at 120° to less than 10 min at 180°, but had little effect on the yield of lactone obtained.

The presence of less than 1% water in the reaction mixture did not seriously interfere with the lactone synthesis. Larger amounts of water, however, tended to increase the reaction times and decrease the lactone yields. The addition of 6% water increased the reaction time fourfold, while the lactone yield was cut in half. The addition of acid anhydrides to control the water content was found to be quite satisfactory, especially for the *in situ* preparations of manganic ion.

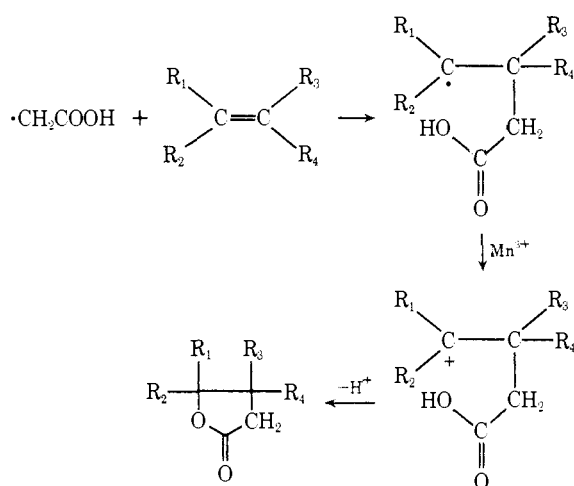
Studies on the reaction of manganic acetate with octene-1 showed little effect on the lactone yield obtained (61-64%) when the manganic ion and olefin concentrations were varied by factors of 4 or 5.

In the lactone synthesis, it was found advantageous to add 10-30% potassium acetate or other carboxylate salt to the reaction mixture. The addition of acetate ion shortened the reaction time by raising the reflux temperature of the reaction mixture and decreased the formation of side products resulting in higher lactone yields. This effect of suppressing side reactions was especially important when high concentrations of a conjugated olefin such as styrene were used. For example, the yield of γ-phenylbutyrolactone prepared *via* Ce(OAc)₄ increased from 13 to 70% upon the addition of 10% KOAc. Similar improvements were observed in the reactions of substituted styrenes with manganic acetate.

Discussion

Mechanism. Previous studies on the thermal decomposition of manganic and ceric acetate^{1,5,6} have demonstrated

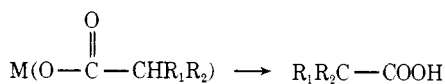
Scheme I



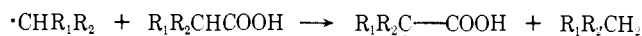
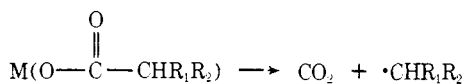
the intermediacy of free carboxymethyl radicals. This has led us to propose the free radical mechanism for the lactone synthesis presented in Scheme I.

The essence of the lactone synthesis lies in the selective formation and the selective oxidation of organic free radicals by metal oxidants. The thermal decomposition of manganic(III), ceric(IV), and vanadium(V) carboxylates, unlike that of the corresponding salts of lead(IV), proceeds *via* the selective and direct generation of carboxymethyl radicals. Our studies on the decomposition of higher valent metal carboxylates in solution have indicated the existence of two distinct modes of decomposition: (1) a carboxyalkyl radical pathway which predominates in the thermal decomposition of manganic, ceric, and vanadium salts, in which the carboxyalkyl radical is formed directly, and (2) a decarboxylative pathway characteristic of lead carboxylates in which the higher valent metal carboxylate decomposes to an alkyl radical and carbon dioxide. In this latter mechanism, the carboxyalkyl radical is then only formed indirectly and nonselectively in a subsequent reaction which involves attack of the alkyl radical on the acid solvent.

(1) Carboxyalkyl radical pathway (Mn^{3+} , Ce^{4+} , V^{5+})



(2) Decarboxylative pathway (Pb^{4+})



The unique mode of thermolysis of manganic, ceric, and vanadium carboxylates accounts for the high yields of lactones obtained and the absence of products derived from alkyl radical attack on the olefin. The absence of significant amounts of CO_2 or methane from the thermolysis of manganic acetate in the presence of an olefin further supports the formation of carboxymethyl radicals directly without the intermediacy of free acetoxy or methyl radicals.

In this lactone synthesis, the absence of any significant polymer formation can be attributed to the selective oxidation of organic free radicals by metal ions. The initially formed carboxymethyl radical is only difficultly oxidized by the metal ion, owing to the electron-withdrawing carboxyl group in the α position,⁸ whereas the radical formed by addition of the carboxyl methyl radical to the olefin is relatively rapidly oxidized to the carbonium ion, which then cycli-

zes to the lactone. This rapid oxidation of the adduct radical is responsible for the absence of significant polymerization during the course of the reaction.

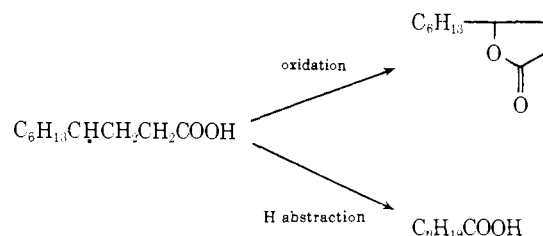
The lactone synthesis depends therefore on five basic mechanistic requirements: (1) the selective direct generation of carboxyalkyl radicals; (2) the difficult oxidation of the initially formed carboxyalkyl radical; (3) the rapid and selective addition of this radical to the olefin; (4) the fast oxidation of the resulting adduct radical to the carbonium ion; and (5) the rapid cyclization of the carbonium ion to the lactone.

The decreased lactone yields obtained in several instances can be directly attributed to problems related to one or more of the mechanistic requirements, as exemplified by the following observations. In the preparation of the octene-1 lactone using manganic acetate, the addition of cupric acetate drastically reduced the yield of lactone obtained. Since cupric ion is known to be an extremely effective oxidant of free radicals,^{9,10} the low yield can be attributed to oxidation of the carboxymethyl radical before it could add to the olefin. Similarly, the low yields of lactones obtained from isobutyric acid may in part be due to the greater ease of oxidation of the tertiary dimethylcarboxymethyl radical by the metal oxidant. The higher lactone yield obtained from octene-1 relative to octene-4 is in large part due to the faster rate of carboxymethyl radical addition to the terminal olefin.

An expected minor side product of the lactone synthesis is the allylic acetate produced by the abstraction of an allylic hydrogen atom by the carboxyalkyl radical. The high yields of γ -lactones produced relative to the allylic acetates, $\sim 30:1$ for β -methylstyrene and $\sim 50:1$ for octene-1, however, clearly demonstrate the great selectivity of the carboxymethyl radical toward addition to the olefin over allylic hydrogen abstraction.

Only very low lactone yields were obtained from olefins such as diethyl maleate and methyl acrylate, and this can be attributed to the difficult oxidation of the adduct radical due to the presence of electron-withdrawing functions in the α position.

The incomplete oxidation of the adduct radical is also responsible for the formation of small amounts of saturated acids, such as decanoic acid from octene-1, as by-products of the lactone synthesis. Apparently under our normal reaction conditions, hydrogen abstraction by the secondary alkyl radical competes only slightly with oxidation by the metal oxidant.¹¹



And finally, an illustration of a problem associated with the last requirement, rapid cyclization of the carbonium ion to the lactone, can be found in the case of heptadiene-1,6

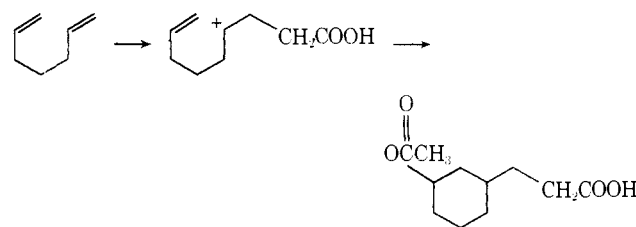


Table III. Relative Reactivity of Various Olefins toward Carboxymethyl Radical Addition at 130°

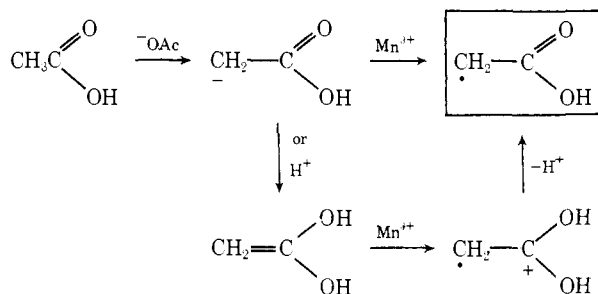
α -Methylstyrene	27		
1,1-Diphenylethylene	19		
Styrene	12		
2-Methylheptene-1	2.4	<i>p</i> -Methylstyrene	1.26
<i>trans</i> - β -Methylstyrene	2.1	<i>p</i> -Bromostyrene	1.04
<i>trans</i> -Stilbene	1.3	<i>m</i> -Bromostyrene	1.01
<i>cis</i> - β -Methylstyrene	1.0	Styrene	1.00 ^b
Octene-1	1.0 ^a		
Cyclooctene	0.78		
<i>cis</i> -Stilbene	0.36		
<i>cis</i> -Octene-4	0.21		
<i>trans</i> -Octene-4	0.20		

^a Octene-1 arbitrarily chosen as standard. ^b Styrene arbitrarily chosen as standard.

which gave a considerably reduced yield of lactone. In this case, a major side product derived from internal addition of the carbonium ion to the remote double bond was isolated.

The Addition of Carboxymethyl Radicals to Olefins. The relative rate of addition of the carboxymethyl radical to various olefins was determined by applying a competitive technique and measuring the relative ratio of the lactones produced (Table III). In general, the reactivity of various olefins towards the addition of the carboxymethyl radical is governed by the stability of the radical intermediate as well as by steric considerations and is similar to what has been observed with other carbon radicals. The greater reactivity of the *trans* isomers of β -methylstyrene ($k_{\text{trans}}/k_{\text{cis}} = 2.1$) and stilbene ($k_{\text{trans}}/k_{\text{cis}} = 3.6$) is comparable with the addition behavior of the methyl radical.¹² The absence of any significant polar effect in the addition reaction of carboxymethyl radicals was indicated by the comparable reactivity of variously substituted styrenes.

On the Direct Formation of Carboxyalkyl Radicals by Manganese(III). The direct formation of carboxyalkyl radicals from carboxylic acids by manganese(III) most probably involves initial enolization of the carboxylic acid followed by electron transfer from either the enol or the enolate anion. This is indicated by the fact that highly enolizable carboxylic acids such as cyanoacetic acid react much more rapidly with manganese(III) than do simple alkyl carboxylic acids. In addition, other highly enolizable compounds, such as ketones, aldehydes, and dialkyl malonates, react very rapidly even at room temperature with manganic acetate in acetic acid. In the reaction of ketones with manganic acetate, the rate of reaction was found to be independent of the manganic ion concentration, first order in ketone concentration, and accelerated by acetate ions. The importance of base-catalyzed enolization in these reactions was further demonstrated by the relative rates of disappearance of *para*-substituted benzyl phenyl ketones, where electron-withdrawing groups increased the reaction rate with manganic acetate.¹⁰ The preference for formation of the least substituted α -keto radical from unsymmetrical ketones¹⁰ is further support for the intermediacy of an enolate anion.



Experimental Section

The commercially available organic and inorganic compounds were purchased in the purest quality obtainable and used without further purification. Manganic acetate dihydrate and anhydrous manganic acetate were prepared by the method described in an earlier publication.⁵

Activated manganese dioxide was prepared by simultaneously adding an aqueous solution of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (166.5 g) and a 40% solution of NaOH (234 ml) to a hot stirring solution of KMnO_4 (192 g) in 1200 ml of water. The solid obtained upon filtration was soluble in glacial acetic acid.

Ceric acetate was prepared by ozonolysis of cerous acetate.⁴

Lactone Synthesis by the Reaction of Manganic Acetate with Olefins. In a typical experiment, a 0.1 *M* solution of the olefin in glacial acetic acid was refluxed under nitrogen with 2 mol equiv of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$, in the presence of added potassium acetate (300 g/l.), until the brown manganic color disappeared. The reaction mixture was diluted with water and extracted several times with ether. In larger runs, it was advisable to remove most of the acetic acid on the rotary evaporator prior to extraction. The ether extracts were then dried and evaporated down. The residue was then analyzed by vapor phase chromatography. Vpc yields were obtained by adding an internal standard such as phenyl benzoate and analyzing on a 12-ft, 10% Silicone SE-30 column in an F&M Model 810 gas chromatograph with dual thermal conductivity detectors. Peak areas were obtained on a Varian Aerograph Model 475 automatic integrator and were corrected for differences in response for the various compounds involved.

Isolation of the pure γ -lactones was generally achieved by distillation, and structural identification was provided by infrared (5.6- μ peak characteristic of γ -lactones) and nmr spectroscopy, elemental analysis, and, occasionally, mass spectroscopy.

Lactones Prepared from Other Acids. For the preparation of lactones derived from acids other than acetic acid, acetic acid was replaced by the desired acid, and KOAc was replaced by the salt of the corresponding acid. For example, 2.1 g of styrene and 11.6 g of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ were refluxed under nitrogen in 200 ml of propionic acid containing 20 g of potassium propionate. In less than 1 hr, a 50% yield of α -methyl- γ -phenylbutyrolactone was obtained. The formula $\text{C}_{11}\text{H}_{12}\text{O}_2$ was indicated by analysis and the compound exhibited a lactone carbonyl infrared band at 5.58 μ . The nmr spectrum contained a methyl doublet at δ 0.88 ($J = 6$ Hz) which was spin decoupled by irradiation at δ 2.25.

Replacement of all the acetic acid was not required for very reactive acids such as cyanoacetic acid. In this case, 0.4 mol of cyanoacetic acid dissolved in 1 l. of acetic acid containing 10% KOAc reacted with 0.1 mol of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ and 0.2 mol of olefin at 50°. After 1 hr, most of the acetic acid was removed on the rotary evaporator, and the residue was extracted several times with ether and water. The ether layers were washed with aqueous sodium carbonate, dried over anhydrous magnesium sulfate, filtered, and stripped. The yields of α -cyano- γ -butyrolactones obtained were generally in the 40–60% range based on oxidant consumed.

Mixtures of acids were also used in the case of succinic acid. Thus, 700 g of succinic acid and 300 g of acetic acid were refluxed with 14 g of monosodium succinate, 40 g of KOAc, 15 g of octene-1, and 54 g of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$. When the reaction was completed, the mixture was diluted with water and extracted with ether. The reaction product, obtained in 25% yield, was recrystallized from petroleum ether and melted at 76–76.5°.

Lactone Synthesis via the *In Situ* Preparation of Manganic Acetate. In a typical experiment, 212 g (0.84 mol) of manganous acetate tetrahydrate was dissolved in 1200 ml of glacial acetic acid by raising the temperature to 90°. At this temperature, 32 g (0.2 mol) of KMnO_4 was added with stirring. When the exothermic reaction had subsided and temperature had again dropped to 90°, 300 ml of acetic anhydride was added followed by 500 g of sodium acetate. Eighty-four grams (0.6 mol) of decene-1 was added, and the reaction mixture was refluxed (~130) until the brown manganic color had disappeared (approximately 1 hr). Extraction and distillation yielded 66.4 g of the pure lactone, γ -*n*-octylbutyrolactone, bp 106° (1.0 mm), which represented a 67% yield based on KMnO_4 .

In an alternate procedure, 110 g of manganous diacetate dihydrate was dissolved in a solution containing 700 ml of glacial acetic

acid, 75 g of potassium acetate, and 75 g of acetic anhydride. The mixture was heated to 95° at which point 19 g of KMnO_4 were added. The resulting manganic acetate solution was then used for the preparation of various lactones.

Relative Reactivity of Various Olefins. Competitive Procedure. In a typical experiment, 20 ml of an acetic acid solution, 0.2 *M* in each of the two olefins under study and 1 *M* in potassium acetate, was mixed with 20 ml of a 0.1 *M* solution of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ in acetic acid, also 1 *M* in KOAc. The reaction mixture was placed in a tube, flushed with nitrogen, and sealed. The reactions were run in a constant-temperature bath maintained at $130 \pm 1^\circ$ for a period of 1–2 hr, by which time the brown manganic color had disappeared.

When the reaction was over, the tube was cooled, and the reaction mixture was diluted with 200 ml of ether. The ether solution was extracted twice with ice–water and three more times with cold saturated sodium bicarbonate solution. The ether extract was then dried over sodium sulfate, and after filtration the ether was removed on a rotary evaporator. The resulting reaction residue was then analyzed by vapor phase chromatography.

The relative amounts of the two lactones formed were determined from the areas of the corresponding vpc peaks, corrected for differences in response for the two compounds. All reactions were run in duplicate and analyzed twice each by vpc.

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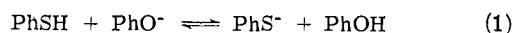
Thermodynamics of Acid–Base Equilibria. V.^{1–4} Ionization of Thiophenol. An Ion Size Effect

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Abstract: The thermodynamic parameters $\Delta\bar{G}^\circ$, $\Delta\bar{H}^\circ$, $\Delta\bar{S}^\circ$, and $\Delta\bar{V}^\circ$ have been determined for the ionization of thiophenol in aqueous solution at 25°. These values have been combined with the literature values for the ionization of phenol in aqueous solution at 25°, and the thermodynamic parameters for the proton transfer reaction, $\text{PhSH} + \text{PhO}^- \rightleftharpoons \text{PhS}^- + \text{PhOH}$, (1), have been calculated. The gas-phase thermodynamic parameters $\Delta G^\circ_1(\text{g})$, $\Delta H^\circ_1(\text{g})$, and $\Delta S^\circ_1(\text{g})$ have been estimated for eq 1 and compared with the corresponding solution parameters. The results are analyzed in terms of current solution theories. The volume change for eq 1 can be adequately accounted for in terms of van der Waals volumes and the calculated electrostriction of the solvent by the anions. The entropy change for eq 1 could not be completely accounted for by any current theory.

Enthalpies, entropies, and volumes of ionization^{5a} provide useful information concerning solute–solvent interactions. Numerous investigators have extensively studied the thermodynamics of ionization of phenol and substituted phenols, as summarized by Larson and Hepler.^{5a} The data indicate that the variation of the $\text{p}K_a$'s of substituted phenols is almost completely due to changes in the entropy of ionization. In contrast, very few reliable data are available on the sulfur analog of phenol, thiophenol. The $\text{p}K_a$ of thiophenol has been investigated by several researchers^{6,7} and is reported to be approximately 6.5. These results show that thiophenol is considerably more acidic than phenol ($\text{p}K_a = 9.97$). The relative acidities are clearly demonstrated in the proton transfer reaction shown in eq 1 for which the aque-



ous Gibbs free energy of proton transfer [$\Delta G^\circ_1(\text{aq})$] is calculated to be -4.75 kcal/mol.

In this study, the thermodynamic parameters $\Delta\bar{G}^\circ$, $\Delta\bar{H}^\circ$, $\Delta\bar{S}^\circ$, and $\Delta\bar{V}^\circ$ have been determined for the ionization of thiophenol in aqueous solution. The values have been combined with the literature values for the ionization of phenol in aqueous solution at 25° to yield the thermodynamic parameters for eq 1. In addition, the gas-phase thermodynamic parameters $\Delta G^\circ_1(\text{g})$, $\Delta H^\circ_1(\text{g})$, and $\Delta S^\circ_1(\text{g})$ have been estimated by a combination of semiempirical (CNDO/2) results and statistical thermodynamic methods. The thermodynamic functions for the proton transfer reaction are analyzed in terms of current theories in order to approach a better understanding of solute–solvent interactions⁵ involved in organic acid–base equilibria.

Experimental Section

The $\text{p}K_a$ of thiophenol was determined spectrophotometrically at the absorbance maximum of the thiophenoxide anion ($37,950 \text{ cm}^{-1}$). The extinction coefficients of thiophenol ($\epsilon_{\text{PhSH}} 560$) and