Acknowledgment.—We are indebted to Dr. R. A. Friedel and Mr. A. G. Sharkey, Bureau of Mines, Pittsburgh, for recording the mass spectra on a Consolidated Electrodynamics Corporation instrument.

Appendix

Let

- T_n be the abundance of the n + 1 peak in the monoisotopic compound containing only C^{12}
- H_n is the abundance of the fragments in the synthetic labeled compound
- X_n and Y_n are parts of a given fragment derived and not derived from the labeled position and calculated as indi-cated in Appendix of the previous investigation.²

We wish to find: H'_n as the abundance of the n+1fragment in a mass region of j carbon atoms not containing any natural C^{13} and $(L - N)C^{13}$ in the central portion. This is the synthetic mass spectrum H_n corrected for natural C¹³. H_n'' is the compound H'_n with 100% C¹³ enrichment in the labeled position.

Assuming no isotope effects, we can write

$$X_n + Y_n = T_n$$
 (1)
 $X_{n-1} + Y_n = H''_n$ (2)

 $X_{n-1} + Y_n = H''_n$

subtracting 2 from 1

 $X_n - X_{n-1} = T_n - H''_n$

since for j = 1 we can derive that

$$H_n = X_n(1-L) + X_{n-1}L + Y(1-N) + Y_{n-1}N$$

Substituting for Y and Y - 1 from eq. 1 we obtain $H_n = X_n(N - L) + X_{n-1}(L - N) + T_n(1 - N) + T_{n-1}N$ Rearranging and substituting from eq. 3 for $(X_n X_n = 1$

$$H_n = (T_n - H''_n)(L - N) + T_n(1 - N) + T_{n-1}N \quad (4)$$

Since a partially labeled compound can be considered a mixture of S_n and H''_n we have

 $H'_n = H''_n(L - N) + T_n(1 - L - N) = (H''_n - T_n)$ $(L - N) + T_n$ (5)

Substituting this equation into 4

$$H_n = (H'_n - T_n) + T_n(1 - N)T_{n-1}N \text{ or } H'_n = H_n + N(T_n - T_{n-1})$$

For j = 2 we derived

$$\begin{aligned} H_n &- X_{n-2}NL + X_{n-1}[N(1-L) + L(1-N)] + \\ & X_n(1-N)(1-L) + Y_{n-2}N^2 + Y_{n-1}2N(1-N) + \\ & Y_n(1-N)^2 \end{aligned}$$

Substituting as before for Y_1 , Y - 1 and Y - 2from eq. 1 and regrouping

$$\begin{aligned} H_n &= (L-N)[(X_n - X_{n-1})(N-1) + (X_{n-1} - X_{n-2}) \\ (-N)] &+ T_{n-2}N^2 + T_{n-1}2N(N-1) + T_n(1-N)^2 \end{aligned} \\ \end{aligned}$$
 Then by eq. 3

$$H_n = (L - N)[(T_n - H''_n)(N - 1) + (T_{n-1} - H''_{n-1}) (-N)] + T_{n-2}N^2 + T_{n-1}2N(N - 1) + T_n(1 - N)^2$$

and by using eq. 4, we obtain

$$H'_{n} = \frac{1}{1-N} \left[H_{n} - NH'_{n-1} - T_{n-2}N^{2} - T_{n-1}N \right]$$

Solve the left of the constant of the left of the left

Similarly for j = 31

$$H'_{n} = \frac{1}{(1-N)^{2}} [H_{n} - H'_{n-1}2N(1-N) - H'_{n-2}N^{2} - T_{n-3}N^{3} - T_{n-2}N^{2} (2-3N) - T_{n-1}N(1-3N) - T_{n-1}N(1-N)^{2}]$$

$$(1-N) + T_{n}N(1-N)^{2}$$

and
$$j = 4$$

 $H'_n = \frac{1}{(1-N)^3} [H_n - H'_{n-1}3N(1-N)^2 - H'_{n-2} \cdot 3N^2 + (1-N) - H'_{n-3}N^3 + T_nN(1-N)^3 - T_{n-1}N(1-N)^2 \cdot (1-4N) - T_{n-2}N^2 \cdot (1-N)(3-6N) - T_{n-3}N^3 - (3-4N) - T_{n-4}N^3 - (3-4N) - (3-4$

However, of $N \ll 1$ we can approximate 1/(1 - 1) $N \rightarrow 1 + N$, $1/(1 - N)^2$ as 1 + 2N and eliminating all powers of N, these equations are reduced to $H'_{n} = H_{n} + N(T_{n} - T_{n-1}) + (j - 1)N(H_{n} - H'_{n-1})$

THE DISSOCIATION CONSTANTS OF *p*-ALKYLMERCAPTOBENZOIC ACIDS

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Received February 19, 1957

Gilman and Webb¹ studied the metallation of anisole and thioanisole by butyllithium and found that anisole undergoes nuclear metallation while, under the same conditions, thioanisole undergoes lateral metallation. The hydrogen atoms of the methyl group in thioanisole are thus more labile than those in anisole. We recently showed² that the methylene group in an arylmercaptoacetic acid is more reactive than that in an aryloxyacetic acid. We suggested³ that the greater reactivity of the methyl group in thioanisole and of the methylene group in arylmercaptoacetic acids might be due to the ability of sulfur to expand its valence shell through hyperconjugation. In an attempt to find if this view can be substantiated by further evidence the apparent dissociation constants of *p*-methyl-, p-ethyl- and p-isopropylmercaptobenzoic acids were determined. The pK_A values of these three acids are $5.80,^4$ 5.71 and 5.66, respectively, at 32°. The dissociation constant thus increases in the order: isopropyl > ethyl > methyl. Considering the inductive and resonance effect of the alkylmercapto group, the order should be reversed. The observed order may be explained by hyperconjugation involving the expansion of the valence shell of sulfur. In the case of p-methylmercaptobenzoic acid the hyperconjugative effect is highest due to the contribution of the structures



The number of such structures progressively decreases to 2 and 1 in *p*-ethyl- and *p*-isopropylmercaptobenzoic acids, thus increasing their ability to dissociate in the same order.

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 $T_{n-4}N^{4}$]

(3)

Experimental

Preparation of Materials. p-Methylmercaptobenzoic Acid.—p-Aminobenzoic acid (17 g.) was diazotized with sodium nitrite (15 g.) and hydrochloric acid (50 ml.) under the usual conditions. The resulting diazonium salt solution was poured into a hot (70°) freshly prepared solution of po-tassium ethyl xanthate (20 g. in 200 ml. of water) containing sodium carbonate (50 g.) to pourolize the acid in the diazosodium carbonate (50 g.) to neutralize the acid in the diazonium salt solution. After the brisk evolution of gases had subsided, the mixture was treated with sodium hydroxide solution (5 g. in 50 ml. of water) and dimethyl sulfate (15.8 g.) and refluxed for 5 hr. On cooling and acidifying with hydrochloric acid, the crude *p*-methylmercaptobenzoic acid separated; yield 16.8 g. (80%). This on recrystallization from ethanol melted at $189-190^{\circ}$. Gattermann⁶ who prepared this acid by oxidizing p-methylmercaptobenzaldehyde

p-Ethylmercaptobenzoic Acid.—This was prepared by the method of Donleavy and English.⁶

p-Isopropylmercaptobenzoic Acid.—The method used for its preparation was the same as that for p-methyl-mercaptobenzoic acid, except isopropyl bromide was sub-stituted for dimethyl sulfate. The yield was almost quantitative. After a number of recrystallizations from methanol, the acid melted at 155-156°.

Anal. Calcd. for $C_{10}H_{12}O_2S$: C, 61.2; H, 6.1. Found: C, 61.4; H, 5.8.

Determination of Acidity Constants of the Acids.-0.001 M solutions of the acids were prepared in 1:1 ethanol-water, free from carbon dioxide. In each case a known volume of the solution was neutralized to the extent of 20, 40, 50 of the solution was neutranized to the extent of 20, 40, so and 60% by using carbonate-free sodium hydroxide solution (0.001 M). The mixture was made up to 100 ml. The pH of the solution at 32° was determined by means of a Cambridge pH meter using the Morton glass electrode. The pK_A values were calculated from the Henderson equa-tion⁷ and are the average of four determinations at 20, 40, 50 and 60% rearrent pixeline. the spread in pK_A for any solid 50 and 60% neutralization; the spread in pK_A for any acid did not exceed by 0.04.

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INFRARED SPECTRA OF METALLIC COMPLEXES. III. THE INFRARED SPECTRA OF METALLIC OXALATES

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In the first paper of this series,¹ we have studied the effect of coördination on the infrared spectra of typical metallic complexes of non-chelated ligands such as ammine, rhodanato and azido complexes.

Some work has been reported on complexes with chelated ligands²⁻⁷; however, most of the bands observed are difficult to assign because of the complicated structures of the molecules. As a consequence, discussions have been limited to a few bands which are relatively sensitive to the kinds of metals. For example, Bellamy and Branch⁴ could

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correlate the stability of metal salicylaldehyde only with the shift of the C=O stretching frequency.

It is anticipated that, as the metal-ligand bond becomes stronger, all the fundamentals of the ligand should be shifted progressively to higher or lower frequencies depending upon their modes of vibration. Therefore we studied the infrared spectra of metallic oxalates since the structure of the oxalate ion is simple, and the assignment of the oxalate ion fundamentals based on the F.G method⁸ is available. In the present paper, we will discuss the relation between the strength of the M-O bond and the direction and magnitude of the shift of each fundamental of the metallic oxalates. Although the infrared spectra of many oxalates already have been measured by Douville, $et \ al.$,² their experimental results are different from ours, and, moreover, no discussion was given on the relation between the stability and the band shift.

Experimental

The oxalates of Al³⁺, Co³⁺, Cr³⁺, Fe³⁺, 9 Cu^{2+,10} Co^{2+,11} and Ni^{2+,12} were prepared according to the literature.

Measurements of infrared spectra were made by a Perkin-Elmer Model 21 double beam infrared spectrophotometer using NaCl and KBr prisms. The Nujol mull technique was employed.

Discussion

The X-ray analysis of sodium oxalate¹⁸ indicates that the oxalate ion is planar and the interatomic distances and angles are



Although the angles of C-C-O_I and C-C-O_{II} are not equal, this might be due to the error of the Xray analysis. Thus we assume that the ion has V_h symmetry. On the other hand, the X-ray data of $K[Cr ox_2(H_2O)_2] \cdot 3H_2O^{14}$ give the dimensions

TABLE I

CLASSIFICATION OF THE 12 FUNDAMENTALS IN OXALATE ION Assignmenth in C. 37. 0 Con

* 6 *	0200	Treat and the state of the Cat
$3 a_g (R)$	3 a1 (R, IR)	ν (C-O), ν (C-C), sym δ (O-
		C-O)
1 a _u (inactive)	$1 a_2 (R)$	Out-of-plane
$2 b_{1g} (R)$	$2 b_1 (R, IR)$	ν (C-O), asym. δ (C-C-O)
1 b _{1u} (IR)	1 b ₂ (R, IR)	Out-of-plane
$1 b_{2g} (R)$	$1 a_2 (R)$	Out-of-plane
$2 b_{2u} (IR)$	$2 a_1 (R, IR)$	ν (C–O), sym. δ (C–C–O)
$0 b_{sg} (R)$	$O b_2 (R, IR)$	
2 b ₂ (IR)	$2 b_1 (R, IR)$	ν (C-O), asym. δ (O-C-O)

b₁ (n,

^a R, Raman active; IR, infrared active. ^b G. Herzberg,

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