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SPECTROPHOTOMETRIC INVESTIGATIONS ON THE SOLVOLYSIS OF TRIPHENYLTIN OXINATE IN METHANOL

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SUMMARY

A detailed analysis of spectrophotometric data on triphenyltin oxinate in methanol and benzene/methanol mixture has revealed the existence of the equilibria:

$$Ph_3SnOx + MeOH \rightleftharpoons Ph_3SnOx \cdot MeOH \rightleftharpoons Ph_3SnOMe + HOx$$

The values of the two equilibrium constants are 5.6×10^{-2} and 4.0×10^{-3}, respectively.

INTRODUCTION

From the similarity of the electronic spectrum of triphenyltin oxinate to that of oxine (8-hydroxyquinoline) in 95% ethanol, a non-chelated tetra-coordinated structure was proposed for this compound by Roncucci *et al.*[1]. However, a penta-coordinated structure has been proposed recently by Okawara *et al.*[2] because the spectrum in cyclohexane showed a ligand band at 370 nm which corresponds to those of other chelated metal oxinates[3-7], rather than that of oxine. These workers attributed the anomalous observations by Roncucci *et al.*[1] to possible hydrolysis in 95% ethanol. However, no detailed investigation of this problem has previously been reported.

Examination of the electronic spectrum of triphenyltin oxinate in a number of solvents in our laboratory has shown that while the spectrum in non-hydroxylic solvents such as carbon tetrachloride, diethyl ether, hexane, benzene, etc., shows the band at the usual position, ca. 370 nm, that in hydroxylic solvents, *e.g.*, methanol, is quite different and is strongly concentration-dependent. Such a drastic change in the spectrum on going from non-hydroxylic to hydroxylic media cannot be attributed to normal solvent effects, especially in view of the fact that the spectra of other phenyltin oxinates such as diphenyltin dioxinate, exhibit very little change in going from carbon tetrachloride to ethanol or methanol. In view of these observations a detailed

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spectrophotometric investigations of this system was considered necessary. Because of the possibility of hydrolysis in aqueous alcoholic solutions, anhydrous solvents were used throughout.

RESULTS AND DISCUSSION

The spectra of triphenyltin oxinate in different solvents are shown in Fig. 1. The spectra in benzene, ether or carbon tetrachloride are all very similar and have absorption peaks at about 360 nm, and the molar extinction coefficients are also almost constant. The data are summarized in Table 1.

The spectrum in methanol solution is quite different. The absorption maximum is shifted to 310 nm, and the molar extinction coefficient shows a gradual increase as the concentration of the solution is lowered (Table 2). At about 10^{-4} *M* concentration, the spectrum, is virtually identical with that of oxine (Fig. 2).

The large shift in the absorption peak cannot be attributed to a solvent effect, as other phenyltin oxinates, *e.g.*, diphenyltin dioxinate, exhibit little change in the spectrum in going from carbon tetrachloride to methanol. Similarly, the apparent deviation from Beer's law is unlikely to be a special feature of triphenyltin oxinate as other oxinates have been found to obey Beer's law. Further, Beer's law is obeyed by

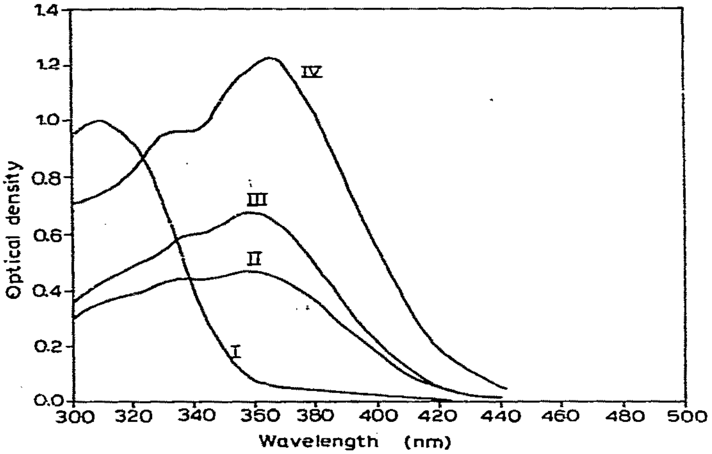


Fig. 1. Absorption spectra of triphenyltin oxinate in different solvents: I. methanol (4.080×10^{-4} *M*); II. benzene (2.167×10^{-4} *M*); III. ether (3.245×10^{-4} *M*); IV. carbon tetrachloride (5.880×10^{-4} *M*).

TABLE 1

ABSORPTION PEAKS AND EXTINCTION COEFFICIENTS FOR TRIPHENYLTIN OXINATE IN DIFFERENT SOLVENTS

Solvent	Concn. (10^{-4} *M*)	λ_{max} (nm)	ε_{max}
CCl_4	5.880	364	2080
$C_2H_5OC_2H_5$	3.245	360	2050
C_6H_6	2.167	360	2170

TABLE 2

MOLAR EXTINCTION COEFFICIENTS FOR TRIPHENYLTIN OXINATE AND OXINE AT DIFFERENT CONCENTRATIONS IN METHANOL

Solute	Concn. (10^{-4} *M*)	ε
Ph_3SnOx	8.160	2080
	4.080	2450
	1.632	2480
	0.816	2550
Oxine	1.553	2570

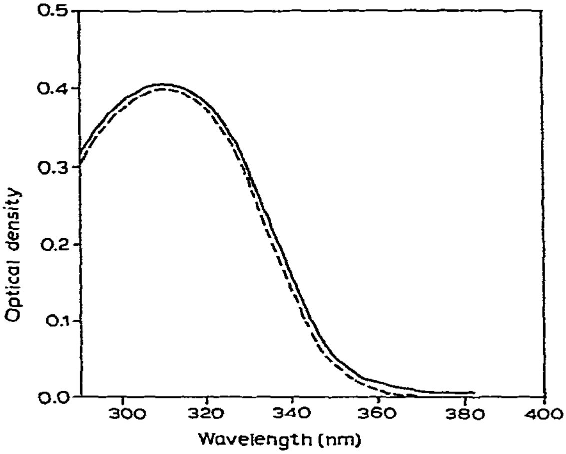


Fig. 2. Absorption spectra of methanolic solution of triphenyltin oxinate (concn. 1.632×10^{-4} *M*, solid line) and oxine (concn. 1.553×10^{-4} *M*, dashed line).

triphenyltin oxinate in non-hydroxilic solvents such as carbon tetrachloride, and diethyl ether.

The considerable change in the spectrum in methanol must thus be attributed to interaction between methanol and triphenyltin oxinate. The following possibilities may be considered:

(*a*). Dissociation of triphenyltin oxinate in methanol, *viz.*,

$$Ph_3SnOx + MeOH \rightleftharpoons Ph_3Sn(MeOH)^+ + Ox^- \quad (1)$$

(*b*). Coordination by solvent molecules

$$Ph_3SnOx + MeOH \rightleftharpoons Ph_3SnOx \cdot MeOH \quad (2)$$

(*c*). Solvolysis. Polar solvents are known to interact with R_3SnCl type compounds[8] leading to ionisation:

$$R_3SnCl + H_2O \rightleftharpoons R_3Sn(OH_2)^+ + Cl^- \quad (3)$$

The first possibility is inconsistent with the fact that oxinate anion (as in solutions of oxine in alkali) is yellow and has absorption peak at 352 nm[9] with a long tail towards the visible region, while triphenyltin oxinate in methanol shows no such band. In fact the molar extinction of triphenyltin oxinate in methanol in the region 360–400 nm decreases with dilution although an increase of molar extinction would be expected if oxinate ion were formed. The low conductivity of triphenyltin oxinate in methanol also rules out ionisation.

The second possibility can also be ruled out, since it can be easily shown that the molar extinction, ε, for an equilibrium of the type (2) is given by:

$$\varepsilon = \varepsilon(\mathrm{Ph_3SnOx}) + K\cdot\varepsilon(\mathrm{Ph_3SnOx\cdot MeOH})\cdot[\mathrm{MeOH}]/(1+K\cdot[\mathrm{MeOH}]) \quad (4)$$

where $K=[\mathrm{Ph_3SnOx\cdot MeOH}]/([\mathrm{Ph_3SnOx}]\cdot[\mathrm{MeOH}])$.

As $[\mathrm{MeOH}] \gg [\mathrm{Ph_3SnOX}]$, the concentration of methanol, [MeOH], remains virtually constant, and ε should therefore be independent of $[\mathrm{Ph_3SnOX}]$. This is inconsistent with the observed data (Table 2).

The solvolysis remains for consideration. The close similarity between the spectrum of free oxine and that of triphenyltin oxinate (Fig. 2) can be taken as an indication of the formation of free oxine (HOx) due to solvolysis. This is confirmed by the fact that addition of oxine solution to a colourless solution of triphenyltin oxinate in methanol immediately restores the yellow colour observed in other solvents. Quantitative spectrophotometric study of the solvolytic equilibria by the addition of oxine in different concentration was not feasible, as it was found that oxine cleaves the Sn–Ph bond leading to the formation of diphenyltin dioxinate. (In fact, we have prepared diphenyltin dioxinate in good yield by refluxing triphenyltin oxinate with oxine in methanol.) As one of the products of solvolysis has been shown to be oxine, the other product is most likely triphenyltin methoxide ($\mathrm{Ph_3SnOMe}$), since the solvents were made anhydrous. This is consistent with the fact that the spectrum of a methanol solution of triphenyltin oxinate at low concentration ($\sim 10^{-4}$ M) is almost superimposable on that of oxine solution (Fig. 2), as since triphenyltin methoxide, like triphenyltin hydroxide, is expected to be non-absorbing above 300 nm.

The mechanism of solvolysis of triphenyltin oxinate is undoubtedly similar to that of the organotin halides and may be represented as:

$$\begin{array}{c}\mathrm{Ph_3SnOx}\\ \uparrow\\ \mathrm{MeOH}\end{array} \rightarrow \mathrm{Ph_3SnOMe + HOx}$$

However, depending on whether an intermediate complex exists in the solution or not, two different sets of equilibrium may be written. These are:

(*i*) $\mathrm{A+B \rightleftarrows X+Y}$ (5)
(*ii*) $\mathrm{A+B \rightleftarrows AB}$ (5a)
$\mathrm{AB \rightleftarrows X+Y}$ (5b)

In these equilibria A, B, AB, X and Y represent $\mathrm{Ph_3SnOx}$, MeOH, $\mathrm{Ph_3SnOx\cdot MeOH}$ (the intermediate), HOx and $\mathrm{Ph_3SnOMe}$, respectively.

It is possible to distinguish between the equilibria (*i*) and (*ii*) by analysis of the spectrophotometric data. For the equilibrium (5), the optical density (D) of the solution will be given by:

$$D = l\cdot(\varepsilon_A\cdot[\mathrm{A}] + \varepsilon_X\cdot[\mathrm{X}]) \quad (6)$$

since the spectrophotometric measurements were carried out in the 370–400 nm region where no component other than triphenyltin oxinate and oxine absorbs. The equilibrium constant, K, will be given by:

$$K = \frac{[\mathrm{X}]\cdot[\mathrm{Y}]}{[\mathrm{A}]\cdot[\mathrm{B}]} = \frac{[\mathrm{X}]\cdot[\mathrm{Y}]}{[\mathrm{A}]\cdot b} \tag{7}$$

where [B] has been replaced by the concentration of methanol in the system, b, as $[\mathrm{B}] \gg [\mathrm{A}]$. The analytical concentration of triphenyltin oxinate, C, in solution is given by:

$$C = [\mathrm{A}] + [\mathrm{X}] = [\mathrm{A}] + K^{\frac{1}{2}}\cdot b^{\frac{1}{2}}\cdot[\mathrm{A}]^{\frac{1}{2}} \tag{8}$$

since, $[\mathrm{X}] = [\mathrm{Y}] = K^{\frac{1}{2}}\cdot b^{\frac{1}{2}}\cdot[\mathrm{A}]^{\frac{1}{2}}$, from eqn. (7). Combination of eqns. (6) and (8), followed by rearrangement leads to eqn. (9):

$$C = \frac{1}{\Delta\varepsilon} + \frac{k^{\frac{1}{2}}\cdot b^{\frac{1}{2}}}{\Delta\varepsilon^{\frac{1}{2}}\cdot\bar{D}^{\frac{1}{2}}} \tag{9}$$

where $\bar{D} = (D - l\cdot\varepsilon_{\mathrm{X}}\cdot C)/l$ and $\Delta\varepsilon = \varepsilon_{\mathrm{A}} - \varepsilon_{\mathrm{X}}$. From eqn. (9) it is apparent that if the methanol concentration is kept constant in a series of solutions in which C is varied then a plot of $C/\bar{D}$ *vs.* $1/\bar{D}^{\frac{1}{2}}$ should give a straight line for equilibrium (5). From the values of the intercept and the slope, K and $\Delta\varepsilon$ may be calculated.

For the equilibria (5a) and (5b), two equilibrium constants K_1 and K_2 may be written, as in eqns. (10) and (11):

$$K_1 = \frac{[\mathrm{AB}]}{[\mathrm{A}]\cdot[\mathrm{B}]} \tag{10}$$

$$K_2 = \frac{[\mathrm{X}]\cdot[\mathrm{Y}]}{[\mathrm{AB}]} \tag{11}$$

As before, [B] may be replaced by 'b', so that

$$[\mathrm{AB}] = K_1\cdot[\mathrm{A}]\cdot[\mathrm{B}] = K_1\cdot b\cdot[\mathrm{A}] \tag{12}$$

Furthermore:

$$[\mathrm{X}] = [\mathrm{Y}] = (K_1\cdot K_2)^{\frac{1}{2}}\cdot b^{\frac{1}{2}}\cdot[\mathrm{A}]^{\frac{1}{2}} \tag{13}$$

In the present case,

$$D = \{\varepsilon_{\mathrm{A}}\cdot[\mathrm{A}] + \varepsilon_{\mathrm{AB}}\cdot[\mathrm{AB}] + \varepsilon_{\mathrm{X}}\cdot[\mathrm{X}]\}\cdot l \tag{14}$$

$$C = [\mathrm{A}] + [\mathrm{AB}] + [\mathrm{X}] = (1 + K_1\cdot b)\cdot[\mathrm{A}] + (K_1\cdot K_2)^{\frac{1}{2}}\cdot b^{\frac{1}{2}}\cdot[\mathrm{A}]^{\frac{1}{2}} \tag{15}$$

Eqns. (14) and (15) may be combined to give eqn. (16):

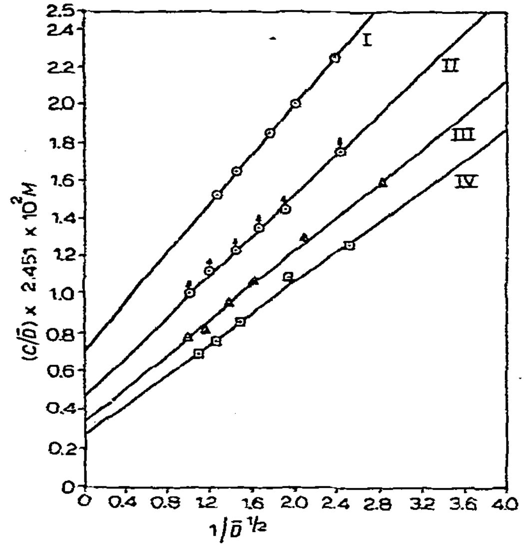
$$\frac{C}{\bar{D}} = \frac{1 + K_1\cdot b}{\Delta\varepsilon} + \frac{(K_1\cdot K_2)^{\frac{1}{2}}\cdot b^{\frac{1}{2}}}{\Delta\varepsilon^{\frac{1}{2}}\cdot\bar{D}^{\frac{1}{2}}} \tag{16}$$

where $\Delta\varepsilon = (\varepsilon_{\mathrm{A}} - \varepsilon_{\mathrm{X}}) + K_1\cdot b\cdot(\varepsilon_{\mathrm{AB}} - \varepsilon_{\mathrm{X}})$ and $\bar{D} = (D - l\cdot C\cdot\varepsilon_{\mathrm{X}})/l$. If the methanol concentration 'b' is kept constant in a set of solutions, the term $\Delta\varepsilon$ then behaves as a constant. Under these circumstances a plot of $C/\bar{D}$ *vs.* $1/\bar{D}^{\frac{1}{2}}$ should be a straight line.

Thus in both the cases $C/\bar{D}$ will vary linearly with $1/\bar{D}^{\frac{1}{2}}$. The two may, however, be distinguished as follows: If the methanol concentration 'b' is varied, it is seen from eqn. (9) that a plot of $(b/\bar{D})^{\frac{1}{2}}$ *vs.* $C/\bar{D}$ should be a straight line whereas this would not be true in the second case, since the first term on the right hand side of eqn. (16) and $\Delta\varepsilon$ both contain '*b*'. However this method would not be very reliable as variation of methanol concentration will lead to a change in the solvent composition and this may change the extinction coefficients. ε_A and ε_X, and thus some deviation from linearity might be expected even if equilibrium (5) is correct. In order to overcome this difficulty, the triphenyltin oxinate concentration, *C*, was varied at fixed methanol concentrations, and a series of such measurements were carried out at different fixed methanol concentration. In each case $C/\bar{D}$ was plotted against $1/\bar{D}^{\frac{1}{2}}$, it may be seen from eqns. (9) and (16) that $(\text{Slope})^2/\text{Intercept}$ for such plots should be a function of the equilibrium constants and the methanol concentration. This may be expressed as the apparent dissociation constant, K', and is given by:

$$K' = K\cdot b \text{ for the equilibrium } (i) \tag{17}$$

$$K' = \frac{K_1\cdot K_2\cdot b}{1+K_1\cdot b} \text{ for the equilibrium } (ii) \tag{18}$$



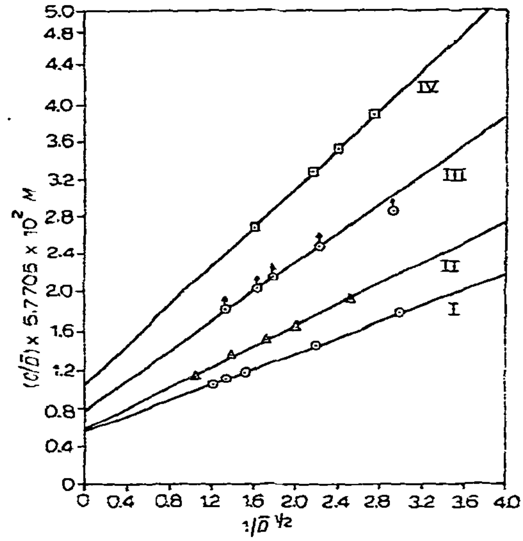


Fig. 3. Plot of $C/\bar{D}$ *vs.* $1/\bar{D}^{\frac{1}{2}}$ for triphenyltin oxinate in methanol at various wavelengths: I. 400, II. 390, III. 380, IV. 370 nm.

Fig. 4. Plot of $C/\bar{D}$ *vs.* $1/\bar{D}^{\frac{1}{2}}$ for triphenyltin oxinate at 400 nm in benzene methanol mixture: I. 2.453 *M*, II. 4.906 *M*, III. 9.812 *M*, IV. 14.719 *M*.

TABLE 3

APPARENT DISSOCIATION CONSTANTS, K' Obtained from Fig. 3.

Wavelength (nm)	$K' \times 10^3$	Average $K' \times 10^3$
370	2.42	
380	2.39	2.41
390	2.45	
400	2.38	

TABLE 4

VARIATION OF K' WITH METHANOL CONCENTRATION AT WAVELENGTHS 390 (a) AND 400 nm (b)

MeOH concn., *b* (*M*)	$K' \times 10^3$		Average $K' \times 10^3$
	a	b	
2.453	0.49	0.51	0.50
4.906	0.81	0.86	0.84
9.812	1.35	1.36	1.36
14.718	1.84	1.81	1.83

Eqn. (18), again, may be written as

$$\frac{1}{K'}=\frac{1}{K_2}+\frac{1}{K_1\cdot K_2}\cdot\frac{1}{b} \tag{19}$$

and eqn. (17) as:

$$\frac{1}{K'}=\frac{1}{K\cdot b} \tag{20}$$

The two cases may now be easily distinguished by plotting $1/K'$ against $1/b$. For mechanism (5), this plot will give a straight line passing through the origin, while for the other mechanism a positive intercept equal to $1/K_2$ would result. From the values of the slope and the intercept both K_1 and K_2 may be calculated.

In Fig. 3 are shown the plots of $C/\bar{D}$ *vs.* $1/\bar{D}^{\frac{1}{2}}$ at different wavelengths. The striking linearity of the plots is consistent with solvolytic equilibria. The apparent dissociation constant K' has been calculated at each wavelengths and are given in Table 3.

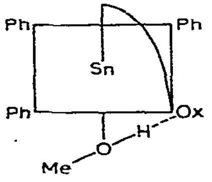
In order to distinguish between two possible solvolytic equilibria (*i*) and (*ii*), it was necessary to determine K' as a function of methanol concentration. In order to obtain these data benzene/methanol mixtures were employed in which the methanol concentration was varied from 2.453 *M* to 14.718 *M*. The plots of $C/\bar{D}$ *vs.* $1/\bar{D}^{\frac{1}{2}}$ at various methanol concentration are shown in Fig. 4 and Fig. 5 and the calculated values of K' are given in Table 4.

Finally, $1/b$ was plotted against $1/K'$ as in Fig. 6. The corresponding data are given in Table 5. The positive intercept in this graph is consistent only with equilibria (5a) and (5b). The values of K_1 and K_2 calculated from Fig. 6 are 5.6×10^{-2} and 4.0×10^{-3} respectively.

The results of the present investigation thus indicate that triphenyltin oxinate undergoes reversible solvolysis in methanol:

$$\mathrm{Ph_3SnOx+MeOH \rightleftarrows Ph_3SnOx\cdot MeOH \rightleftarrows Ph_3SnOMe+HOx}$$

It is interesting to note that Prince[8] has suggested the formation of an intermediate complex $R_3SnX\cdot H_2O$ in the hydrolysis of R_3SnX compounds, although no direct evidence for such complex was available for these systems. The present investigation strongly supports the existence of such intermediates. Although nothing can be said about the structure or configuration of the intermediate $Ph_3SnOx\cdot MeOH$, it is most likely a hexa-coordinated complex, formed by coordination through the oxygen atom. The hydrogen atom of the hydroxyl group of methanol may be bonded to the oxygen atom of oxinate group as depicted in (I), thereby making the structure ideal for breakdown into Ph_3SnOMe and HOx.



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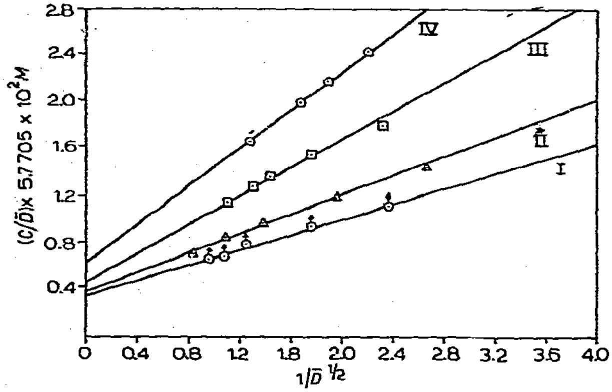

Fig. 5. Plot of $C/\bar{D}$ vs. $1/\bar{D}^{\frac{1}{2}}$ for triphenyltin oxinate at 390 nm in benzene/methanol mixture: I. 2.453 *M*, II. 4.906 *M*, III. 9.812 *M*, IV. 14.719 *M*.

Incidentally, the ease with which triphenyltin oxinate is converted into diphenyltin dioxinate by reaction with oxine may be explained by the formation of a complex $Ph_3SnOx \cdot HOx$, similar to (I). However, since the Ph–Sn bond is cleaved to give diphenyltin dioxinate and benzene the hydrogen atom of the attacking reagent (HOx) is likely to be oriented towards the phenyl group, rather than the oxygen atom of the oxinate group. This does not, however, rule out the possibility of hydrogen-bonded structure similar to (I), since this will simply lead to exchange of the oxinate groups between oxine and triphenyltin oxinate. The difference in the behavior of methanol and oxine may attribute to the chelating tendency of the latter, which will facilitate the breaking of the polar Sn–Ph bond by orienting the $H^{\delta+} - Ox^{\delta-}$ dipole properly to yield a hexa-coordinated structure. In view of the stability of the hexa-coordinated organotin complexes such a process is quite acceptable.

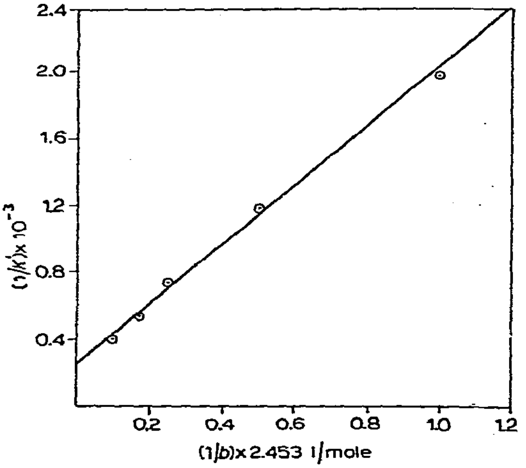

Fig. 6. Variation of the apparent dissociation constant, *K'*, with methanol concentration, *b*.

TABLE 5

VARIATION OF $1/K'$ WITH $1/b$

$1/b$ (0.4077 M)	$(1/K') \times 10^{-3}$
1.000	2.00
0.500	1.19
0.250	0.74
0.167	0.55
0.100	0.41

EXPERIMENTAL

Triphenyltin oxinate was prepared by treatment of bis(triphenyltin) oxide with oxine in methanol. The product was recrystallised several times from methanol and dried in vacuum for 24 h: m.p. 150°. (Found: C, 65.01; H, 4.25; N, 3.10. $C_{27}H_{21}ONSn$ calcd.: C, 65.64; H, 4.28; N, 2.84%.)

All solvents used were of E. Merck, Pro-Analysis-grade and were dried by standard procedures.

Optical densities were measured by Carl Zeiss VSU-1 spectrophotometer using 1 cm quartz cells. The methanol concentration was varied over a wide range, from 2.453 M in benzene to 24.53 M (pure methanol). The optical densities recorded at 390 and 400 nm were mainly used for calculations, since the absorptions due to oxine and triphenyltin methoxide are negligible in this region at the concentration range employed.

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