

TABLE 2 — CONTRIBUTION OF THE SUBSTITUENT IN BENZOYL CHLORIDE AND ANILINE TO THE ACTIVATION ENERGY

Substituent group	ΔE^\ddagger (cal mole ⁻¹)	
	Benzoyl chloride	Aniline
<i>o</i> -Chloro-	-900	+2980
<i>p</i> -Chloro-	-400	+930
<i>m</i> -Nitro-	-960	+3040
<i>p</i> -Nitro-	-1700	+4430
<i>m</i> -Bromo-	-740	+1740
<i>m</i> -Methoxy-	-200	—
<i>p</i> -Methoxy-	+900	—

when plotted against $\log k_{20}$ gives a linear plot with the slope $\approx 2.303 RT$, indicating that for these compounds the entropy of activation is constant. The variations in the velocity constant at a given temperature caused by different substituents in benzoyl chloride are due to the changes in the energy of activation.

The energy of activation of benzoyl chloride being 7600 cal g⁻¹ mole⁻¹, the changes in activation energy (ΔE^\ddagger) caused by various substituents present in substituted benzoyl chlorides have been calculated and the results obtained are given in Table 2. The theoretical values for the activation energies of di- and tri-substituted benzoyl chlorides have been calculated by the addition of the value of ΔE for the substituent groups to the value of activation energy of benzoyl chloride. The value of 2,4-dichlorobenzoyl chloride and 3,4,5-trimethoxy benzoyl chloride have been calculated in the following manner:

(i) Energy of activation of 2,4-dichlorobenzoyl chloride $7600-900-400 = 6300$ cal g⁻¹ mole⁻¹ (experimental value = 6900 cal⁻¹ mole⁻¹) and (ii) energy of activation of 3,4,5-trimethoxybenzoyl chloride $7600-200+900-200 = 8100$ cal g⁻¹ mole⁻¹ (experimental value = 8000 cal g⁻¹ mole⁻¹).

Thus experimental values of energy of activation of di- and tri-substituted benzoyl chlorides are in good agreement with the calculated values. It is interesting to compare the effect of substituents in aniline and in benzoyl chloride on the reaction rate. It is observed (Table 2) that *ortho*-chloro group in the benzoyl chloride decreases the energy of activation, whereas the *o*-chloro group in aniline increases the energy of activation. In the case of *para*-methoxybenzoyl chloride the energy of activation is increased by 900 cal mole⁻¹. As the methoxy group increases the quinonoid structure in both the initial and transitional state of benzoyl chloride, it will therefore increase the activation energy, which has actually been observed.

The plot of dipole moments of substituted benzoyl chlorides versus energies of activation is linear in conformity with the observations of Nathan and Watson⁶ and Grant and Hinshelwood⁷.

This reaction studied also fits well with Hammett's equation⁸. The positive slope value (+1.406) for the Hammett plot indicates that the reaction is aided by the electron withdrawing group in benzoyl chloride.

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Some Novel Di- & Tetra-cyclopentadienyltungsten(VI) & Di- & Tetra-indenyltungsten(VI) Oxides & Sulphides

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Some new di- and tetra-cyclopentadienyltungsten(VI) and di- and tetra-indenyltungsten(VI) oxides and sulphides have been prepared and characterized on the basis of analytical and IR data. Structures with σ - and π -bonded rings, which are not in the same plane, are proposed.

DICYCLOPENTADIENYL- and diindenyltungsten(VI) oxydichlorides¹ and their pseudohalide derivatives² have been reported in literature. Tetracyclopentadienyl- and tetraindenyltungsten(VI) oxides³ are also mentioned in the literature, but there is no reference about the preparation and characterization of the di- and tetra-cyclopentadienyl- and indenyltungsten(VI) sulphides and oxides. This note describes the preparation and characterization of these compounds.

All the reactions were carried out in dry atmosphere. Tetrahydrofuran was purified and dried before use by distillation over lithium aluminium hydride. Freshly distilled cyclopentadiene and indene were used as such or for the preparation of their sodium salts. Tungsten was estimated as WO₃, carbon and hydrogen were estimated by microanalytical methods and sulphur was estimated as BaSO₄. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer model-137 in KBr.

WS₃ (chocolate colour) was prepared by passing H₂S through ammonium tungstate solution and acidifying the resulting yellow thiotungstate solution. WS₂Cl₂, (C₅H₅)₂WOCl₂ and (C₉H₇)₂WOCl₂ were prepared as described in literature^{4,5}. WO₂Cl₂ (yellow crystals) was prepared by exposing the scarlet red crystals of WOCl₄ to dry atmosphere till they turned yellow and then purified by sublimation.

Tetracyclopentadienyltungsten(IV) sulphide — To a suspension of WS₃ (1.12 g, 0.004 mole) in tetrahydrofuran (100 ml) were added freshly distilled cyclopentadiene (1.2 ml, 0.017 mole) and diethyl-

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TABLE 1 — CHARACTERIZATION DATA OF THE COMPOUNDS

Compound	Colour	Found (calc.), %			
		W	C	H	S
(C ₅ H ₅) ₄ WS	Black	38.57 (38.65)	50.21 (50.42)	4.25 (4.20)	6.75 (6.72)
(C ₉ H ₇) ₄ WS	do	27.31 (27.22)	64.13 (63.90)	4.08 (4.14)	4.68 (4.73)
(C ₅ H ₅) ₂ WS ₂	Brown	48.53 (48.67)	31.63 (31.74)	2.69 (2.64)	16.84 (16.93)
(C ₉ H ₇) ₂ WS ₂	do	38.37 (38.50)	45.37 (45.18)	2.96 (2.92)	13.33 (13.40)
(C ₅ H ₅) ₂ WO ₂	Light brown	53.33 (53.18)	34.36 (34.68)	2.86 (2.89)	—
(C ₉ H ₇) ₂ WO ₂	Brown	41.39 (41.25)	48.30 (48.43)	3.18 (3.13)	—
(C ₅ H ₅) ₂ WOS	do	50.63 (50.83)	33.03 (33.14)	2.81 (2.76)	8.93 (8.83)
(C ₉ H ₇) ₂ WOS	Dark brown	39.69 (39.82)	46.63 (46.75)	3.06 (3.03)	7.03 (6.92)

amine (20 ml). The mixture was refluxed at 65-70° till the evolution of H₂S gas ceased (36-38 hr) and then filtered. THF from the clear brown filtrate was distilled off *in vacuo* and the brown residue repeatedly washed with cold ether-pet. ether when a dark brown (almost black) crystalline solid was left. The tetraindenyl compound was similarly prepared.

Dicyclopentadienylytungsten(VI) disulphide — To WS₂Cl₂ (1.27 g, 0.004 mole) in THF (100 ml) was added sodium cyclopentadienide (0.80 g, 0.009 mole). The mixture was refluxed for 8-9 hr under dry conditions and then filtered. The solvent was removed from the filtrate *in vacuo*. The brownish residue was extracted with cold ether-pet. ether when a brown solid with a characteristic odour was obtained. The diindenyltungsten(VI) disulphide was prepared in a similar way. Dicyclopentadienyl/diindenyltungsten(VI) dioxides were prepared by a similar procedure using WO₂Cl₂ instead of WS₂Cl₂.

Dicyclopentadienylytungsten(VI) oxide sulphide — To a solution of dicyclopentadienylytungsten(VI) oxydichloride (1.0 g, 0.0025 mole) in THF (90 ml) was added sodium sulphide (0.24 g, 0.003 mole) and the reaction mixture stirred in dry atmosphere at room temp. for 2 hr. It was then filtered and the clear filtrate evaporated to dryness *in vacuo* leaving a brownish pasty residue. This was washed repeatedly with ether-pet. ether when a brownish crystalline residue was obtained.

The diindenyl compound was prepared similarly.

The compounds are light brown to dark brown in colour. The sulphides possess a peculiar odour. They are sensitive towards moisture but are stable in dry and inert atmosphere. They are soluble in common organic solvents but are insoluble in water. They are non-volatile and do not sublime even under reduced pressure but decompose on heating. They are readily hydrolysed on heating with water or dilute mineral acids, H₂S is liberated in the case of sulphide complexes. Colour and analytical data of the compounds are given in Table 1.

Characteristic bands for cyclopentadienyl/indenyl rings^{6,7} appear in the IR spectra of the present compounds. The IR spectra of (C₅H₅)₄WS and

(C₉H₇)₄WS are comparable with those of (C₅H₅)₄WO and (C₉H₇)₄WO (ref. 8) pointing out similarities in their structures. The IR spectra of the present compounds indicate the existence of σ -bonded as well as π -bonded rings as in the case of tetracyclopentadienyl derivatives of Ti, Zr, Hf, Nb, Ta, and Mo⁹ in which two cyclopentadienyl rings are σ -bonded and the other two π -bonded to the central metal ion. The appearance of a band in the C-H stretch region around 3100* and one or two more weak absorptions, a band of medium to weak intensity at 1610-1640 possibly due to ν C=C and a strong band around 740 support this conclusion. The last two bands are not observed in the IR spectra of π -cyclopentadienyl derivatives of metals.

Except for the differences in ν M-O and ν M-S, the IR spectra of (C₅H₅)₂WO₂ and (C₉H₇)₂WO₂ are quite comparable with those of (C₅H₅)₂WS₂ and (C₉H₇)₂WS₂. The presence of a single broad band of medium intensity around 1040 is more in accord with a geometry involving parallel cyclopentadienyl or indenyl rings¹⁰.

The IR spectra of (C₅H₅)₂WOS and (C₉H₇)₂WOS are also comparable to the IR spectra of (C₅H₅)₂WO₂ and (C₉H₇)₂WO₂. Thus, IR spectra indicate an overall structure involving canted cyclopentadienyl or indenyl rings as have been found in the case of (C₅H₅)₂MoH₂, (C₅H₅)₂TiCl₂ and (C₅H₅)₂ZrCl₂ (refs. 11, 12). The appearance of characteristic doublet of medium intensity around 1050 and two medium intensity bands around 850-890 which are associated with the ring deformations in the compounds having this geometry support the above conclusion.

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*IR bond positions in cm⁻¹.

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Tin(IV) Halide Complexes of Some Thiosemicarbazides

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Complexes of tin(IV) halides with 4-phenylthiosemicarbazide ($H_2N-NH-CS-NHC_6H_5$, PTSC), 1-formyl-4-phenylthiosemicarbazide ($HCO-NH-NH-CS-NHC_6H_5$, PPTSC), 1-acetyl-4-phenylthiosemicarbazide ($CH_3CO-NH-NH-CS-NHC_6H_5$) and 1-isonicotinyl-4-phenylthiosemicarbazide ($C_6H_4NCONH-NH-CS-NHC_6H_5$, IPTSC) have been prepared and characterized on the basis of elemental analysis, molar conductance and infrared spectral measurements.

In a previous paper we reported the preparation and characterization of several tin(IV) chloride complexes with some 1,4-disubstituted thiosemicarbazides¹. Some more complexes of SnX_4 ($X = Cl, Br$ or I) with a few other 1,4-substituted thiosemicarbazides have now been prepared.

4-Phenylthiosemicarbazide (PTSC), 1-formyl-4-phenylthiosemicarbazide (FPTSC), 1-acetyl-4-phenylthiosemicarbazide (APTSC) and 1-isonicotinyl-4-

phenylthiosemicarbazide (IPTSC) were prepared as described by Jensen *et al.*².

Preparation of the complexes — (a) The 1:1 adducts of the type $SnCl_4 \cdot L$ (where $L = PTSC, FPTSC, APTSC$ and $IPTSC$) were precipitated on refluxing the chloroform solution/suspension of tin(IV) chloride and the respective ligands in 3:2 molar ratio for 48 hr. (b) The compounds of the type $SnCl_3(L-H)$ (where $L = PTSC, FPTSC$ and $APTSC$) were obtained by the addition of pet. ether to the filtrate in (a) above after filtering off the precipitates. (c) $SnBr_4 \cdot FPTSC$ and $SnI_4 \cdot FPTSC$ were obtained on mixing the chloroform solution/suspension of tin(IV) halides and the ligand in 3:2 molar ratio followed by stirring at room temperature for 48 hr. (d) $SnBr_3(FPTSC-H)$ was precipitated by refluxing the chloroform solution/suspension of $SnBr_4$ and $FPTSC$ in 3:2 molar ratio while $SnI_3(FPTSC-H)$ was precipitated by adding petroleum ether to the filtrate obtained after separating the precipitate of $SnI_4 \cdot FPTSC$ as described under (c). (e) $SnX_2(FPTSC-2H)$ ($X = Br$ or I) were obtained by refluxing a mixture of chloroform solution/suspension of tin(IV) halide and the ligand in 3:2 molar ratio for 48 hr. The precipitate formed was filtered off and the complexes obtained by adding pet. ether to the filtrate.

All the above complexes were washed with $CHCl_3$ and petroleum ether till free from unreacted tin(IV) halides and dried *in vacuo*. All possible precautions were taken to exclude contact with atmospheric moisture during the synthesis of the complexes.

The details of the analytical procedure and the physico-chemical measurements of the complexes were the same as described earlier¹. The relevant characterization data are given in Table 1.

All the complexes prepared in the present study are insoluble in benzene, chloroform, carbon tetrachloride, petroleum ether and slightly soluble in

TABLE 1 — COLOUR AND ANALYTICAL DATA OF THE COMPLEXES

Complex	Colour	m.p. (°C)	Tin (%)	Halogen (%)	Nitrogen (%)
$SnCl_4 \cdot PTSC$	Light yellow	275	28.1 (29.7)	32.9 (33.3)	10.1 (9.8)
$SnCl_3(PTSC-H)$	Yellow	190	31.0 (30.2)	26.5 (27.4)	10.5 (10.7)
$SnCl_4 \cdot APTSC$	Light yellow	150	25.7 (25.1)	29.6 (30.1)	9.2 (8.9)
$SnCl_3(APTSC-H)$	do	175	27.7 (27.2)	24.2 (24.6)	9.9 (9.7)
$SnCl_4 \cdot IPTSC$	do	210	22.6 (22.2)	26.3 (26.6)	8.1 (7.9)
$SnCl_4 \cdot FPTSC$	Dirty white	235	26.3 (25.9)	32.0 (31.3)	9.1 (9.2)
$SnCl_3(FPTSC-H)$	Yellow	> 350	28.5 (28.1)	24.8 (25.4)	10.2 (10.0)
$SnBr_4 \cdot FPTSC$	do	162	19.0 (18.6)	50.1 (50.6)	7.0 (6.6)
$SnBr_3(FPTSC-H)$	Deep yellow	267	22.0 (21.4)	42.8 (43.5)	7.7 (7.6)
$SnBr_2(FPTSC-2H)$	do	135	25.5 (25.0)	33.2 (34.0)	8.7 (9.0)
$SnI_4 \cdot FPTSC$	Yellowish brown	120	14.8 (14.3)	61.2 (61.2)	5.5 (5.1)
$SnI_3(FPTSC-H)$	do	160	17.6 (17.0)	54.2 (55.0)	6.3 (6.1)
$SnI_2(FPTSC-2H)$	Pinkish brown	145	21.4 (20.9)	44.2 (45.0)	7.9 (7.4)