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Reaction of Titanium Tetrahalides with Phenylhydrazones

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Titanium tetrafluoride reacts with benzaldehyde phenylhydrazone to yield 1 : 1 adduct and with benzophenone phenylhydrazone 1 : 2 as well as 2 : 1 adducts, while other tetrahalides form 1 : 1 adducts with both the phenylhydrazones. All these complexes are coloured and stable at room temperature. The infrared spectral studies of phenylhydrazones and their titanium (IV) complexes have been made in the 4000—200 cm^{-1} region.

Snyder and Smith[1] have investigated the reactions of boron trifluoride with a number of phenylhydrazones containing α-methylene group and they showed that these reactions lead to the formation of indoles presumably through the intermediate formation of 1 : 1 adducts.

Recently Aggarwal and Makhija[2] in this laboratory prepared 1 : 1 adducts of tin tetrachloride with benzaldehyde phenylhydrazone and studied their structures from infrared spectral measurements. This work has now been extended to the reactions of titanium tetrahalides and the results obtained are described in the present communication.

Experimental

Titanium tetrahalides and organic solvents were purified and made anhydrous by standard literature methods. Benzaldehyde phenylhydrazone[3] and benzophenone phenylhydrazone[4] were prepared as described in literature and recrystallized from methanol (mp 157°C) and ethanol (mp 105°C) respectively.

Preparation of Complexes. *i) Titanium Tetrafluoride - Benzaldehyde Phenylhydrazone Complex.* 1—5% tetrahydrofuran solutions of TiF_4 and phenylhydrazone were mixed together and shaken vigorously. The reaction mixture was refluxed for 30 min and excess of solvent removed. The greenish-yellow solid mass thus obtained was washed repeatedly to remove excess of the base, and dried *in vacuo*.

ii) Titanium Tetrafluoride - Benzophenone Phenylhydrazone Complexes. Greenish-brown titanium tetrafluoride-benzophenone phenylhydrazone complex was prepared in a similar way as described above. Another complex (brown) was isolated from the filtrate of the above complex by the removal of excess of the solvent and washing the residual solid with a mixture of chloroform and tetrahydrofuran.

iii) Titanium Tetrachloride - Phenylhydrazone Complexes. On adding dropwise (1—5%) solution of phenylhydrazone in chloroform to a solution of titanium tetrachloride in the same solvent, coloured precipitate was obtained which was allowed to settle for several hours, filtered, washed and dried under reduced pressure.

iv) Titanium Tetrabromide - Phenylhydrazone Complexes. These complexes were prepared just like the titanium tetrachloride complexes.

No definite complexes of titanium tetraiodide with phenylhydrazones could be isolated from reactions carried out in chloroform and benzene solutions.

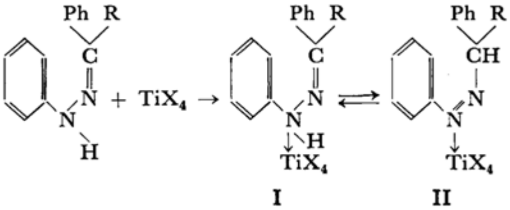
Complexes thus prepared were analysed for titanium, halogen, and nitrogen. Analytical results and general behaviour of the complexes are given in Table 1.

Infrared spectra measurements were carried out on a Beckman infrared spectrophotometer, Model IR-8. The spectra were recorded in Nujol mulls using sodium chloride plates. The far infrared spectra were taken on a Perkin Elmer-621 spectrophotometer in Nujol mulls using cesium iodide cells. The results obtained are included in Tables 2 and 3.

Discussion

Titanium tetrafluoride reacts with benzaldehyde phenylhydrazone to yield 1 : 1 adduct and with benzophenone phenylhydrazone 1 : 2 as well as 2 : 1 adducts, while other tetrahalides form 1 : 1 adducts with both the phenylhydrazones.

Titanium tetrahalides produce intense coloration with phenylhydrazones. The appearance of colour probably may be due to the existence of an equilibrium between the colourless phenylhydrazone and coloured phenylazo tautomer depicted below as titanium tetrahalide adducts:



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[2] R. C. Makhija, "A study of some silicon and tin tetrahalides with hydrazine and its derivatives," Ph. D. thesis, Univ. of Lucknow (1966).

[3] F. G. Mann and B. S. Saunders "Practical Organic Chemistry," Longman, Green & Co., Ltd., 4th Edition, London (1960), p. 227.

[4] F. G. Mann and B. S. Saunders, *ibid.*, p. 343.

TABLE 1. ANALYTICAL DATA AND GENERAL BEHAVIOUR OF COMPLEXES

Molar ratio TiX_4 : Base taken for reaction	Composition of the reaction product formed	% Found			% Calcd			Appearance and solubility	Temperature of decomposition (°C)	Magnetic behaviour
		Ti	Halogen	N	Ti	Halogen	N			
1 : 2	$TiF_4 \cdot C_6H_5CH{=}NNHC_6H_5$	15.3	23.8	9.0	15.00	23.50	8.75	greenish yellow solid, hygroscopic, s in $CHCl_3$, CCl_4, C_6H_6, $C_6H_5NO_2$	turns green at 130	diamagnetic
1 : 2	$(TiF_4)_2 \cdot (C_6H_5)_2C{=}NNHC_6H_5$	18.5	27.9	—	18.46	29.23	—	greenish brown solid, sensitive to moisture, s in THF, $C_6H_5NO_2$, i. in $CHCl_3$, CCl_4	turns dark brown at 144	diamagnetic
1 : 2	$TiF_4 \cdot 2(C_6H_5)_2C{=}NNHC_6H_5$	6.4	9.9	8.55	7.18	11.37	8.38	brown solid, sensitive to moisture, s in THF, $C_6H_5NO_2$, i in $CHCl_3$, CCl_4, C_6H_6	melts at 125 with change in colour	diamagnetic
1 : 2	$TiCl_4 \cdot C_6H_5CH{=}NNHC_6H_5$	12.7	37.0	—	12.44	36.75	—	brown solid, hygroscopic and fuming, i in $CHCl_3$, CCl_4, C_6H_6	turns black at 125	diamagnetic
1 : 2	$TiCl_4 \cdot (C_6H_5)_2C{=}NNHC_6H_5$	10.9	30.7	—	10.39	30.70	—	violet solid, hygroscopic i in $CHCl_3$, CCl_4, C_6H_6	—	diamagnetic
1 : 2	$TiBr_4 \cdot C_6H_5CH{=}NNHC_6H_5$	8.8	56.5	—	8.51	56.88	—	red solid, hygroscopic and fuming, i in $CHCl_3$, CCl_4, C_5H_6, dissolves in THF giving green solution.	turns black at 105	diamagnetic
1 : 2	$TiBr_4 \cdot (C_6H_5)_2C{=}NNHC_6H_5$	7.8	50.5	—	7.50	49.97	—	dark brown solid, i in $CHCl_3$, CCl_4, C_6H_6	turns black at 88	diamagnetic

Abbreviations: THF, tetrahydrofuran; s, soluble, i; insoluble.

TABLE 2. ASSIGNMENT OF IMPORTANT BANDS IN THE SPECTRA OF PHENYLHYDRAZONES AND THEIR TITANIUM TETRAHALIDE COMPLEXES

Compound	ν(N–H) (cm^{-1})	ν(C=N) (cm^{-1})	Aromatic ring vibration and/or ν(N=N) (cm^{-1})	ν(C–N) (cm^{-1})	ν(N–N) (cm^{-1})
$C_6H_5CH{=}NNHC_6H_5$	3290 m, 3090 m	1652 w, 1635 w	1600 s, 1588 s, 1562 s	1298 m, 1285 m, 1258 s	928 m, 878 w
$TiF_4 \cdot C_6H_5CH{=}NNHC_6H_5$	3290 m, 3150 s	1652 w, 1635 w, 1612 m	1598 m, 1578 m, 1570 m, 1565 m	1300 m, 1262 m	920 m, 885 m, b
$TiCl_4 \cdot C_6H_5CH{=}NNHC_6H_5$	—	1650 w, 1632 w, 1612 m	1590 m, 1572 m, 1565 m	1292 w	—
$TiBr_4C_6H_5CH{=}NNC_6H_5$	—	1658 vw, 1638 vw	1560 m, b	—	—
$(C_6H_5)_2C{=}NNHC_6H_5$	3310 m, 3110 m	1650 w, 1632 w	1595 s, 1572 m,	1305 w, 1275 w	960 m, 880 m
$(TiF_4)_2 \cdot (C_6H_5)_2C{=}NNHC_6H_5$	3290 m, b 3138 m	1620 w	1598 w, 1572 w, 1568 w	1305 w, 1290 w	955 m, 890 m
$TiF_4 \cdot 2(C_6H_5)_2C{=}NNHC_6H_5$	3310 m	—	1585 m	1302 w, 1285 w	955 m
$TiCl_4 \cdot (C_6H_5)_2C{=}NNHC_6H_5$	—	1650 w, 1632 w, 1615 w	1585 w, 1572 w, 1568 w	1285 w	—
$TiBr_4 \cdot (C_6H_5)_2C{=}NNHC_6H_5$	—	—	1595 s, b	—	—

TABLE 3. FAR INFRARED SPECTRAL RESULTS OF PHENYLHYDRAZONES AND THEIR TITANIUM TETRAHALIDE COMPLEXES

Compound	ν(Ti–X) (cm^{-1})	ν(Ti–N) (cm^{-1})	Ligand bands, (cm^{-1})
$C_6H_5CH{=}NNHC_6H_5$	—	—	685 s, 662 w, 638 m, 628 m, 608 m, 500 s, 438 m, 388 m, 345 w, 318 w, 285 w, 258 m
$TiF_4 \cdot C_6H_5CH{=}NNHC_6H_5$	630 s, 575 s, b	515 s	695 s, 280 s, 268 s, 258 s
$TiCl_4 \cdot C_6H_5CH{=}NNHC_6H_5$	395 m, 298 m	570 w	675 m, b, 325 m, b, 272 m, 242 m
$TiBr_4 \cdot C_6H_5CH{=}NNHC_6H_5$	320 m,	513 w	690 s, b, 372 m, b
$(C_6H_5)_2C{=}NNHC_6H_5$	—	—	652 m, 652 m, 560 w, 502 w, 435 m, 370 w, 345 w, 322 w, 261 m, 250 m, 242 m
$TiF_4 \cdot 2(C_6H_5)_2C{=}NNHC_6H_5$	658 m, 560 m	508 m	440 m
$(TiF_4)_2 \cdot (C_6H_5)_2C{=}NNHC_6H_5$	660 m, 552 m	515 m	695 m, 685 m, 350 w, 270 w, 240 w
$TiCl_4 \cdot (C_6H_5)_2C{=}NNHC_6H_5$	385 m	565 m, b	375 w, 365 w
$TiBr_4 \cdot (C_6H_5)_2C{=}NNHC_6H_5$	315 m	515 w	678 s, b, 555 m, 382 w, 275 w.

The adducts are intractable, insoluble in common organic solvents and do not possess sharp melting points.

There are two sites for coordination in phenylhydrazones *viz.*, N^I and N^{II} as shown below:

$$\underset{\text{(I)}}{R_1R_2C{=}N^{II}{-}N^IHC_6H_5} \rightleftarrows \underset{\text{(II)}}{R_1R_2CHN^{II}{=}N^IC_6H_5}$$

In titanium tetrahalide complexes of phenylhydrazones, one would expect changes in N–H, N–N, C=N and /or N=N and Ti-X stretching frequencies as compared with the location of these bands in the parent bases and Lewis acids, and appearance of new band characteristic of ν(Ti-N).

N–H Stretching Bands. Spectra of benzaldehyde and benzophenone phenylhydrazones recorded in the present work contain two bands at 3290, 3090 cm^{-1} and 3310, 3110 cm^{-1} respectively assigned to N-H stretching modes.[5,6]

A negative shift in ν(N–H) would be expected if coordination takes place through N^I of the isomer-I. An intramolecular change in phenylhydrazones would yield isomer-II containing no >NH group and hence the infrared spectra of this isomer and its complexes should show no absorptions characteristic of >NH group.

The presence of N-H stretching bands in the spectra of $TiF_4 \cdot C_6H_5CH{=}NNHC_6H_5$, $(TiF_4)_2 \cdot (C_6H_5)_2C{=}NNHC_6H_5$, and $TiF_4 \cdot 2(C_6H_5)_2C{=}NNHC_6H_5$, therefore, indicates that the adducts are formed mainly with tautomeric form-I.

In the infrared spectra of titanium tetrachloride and tetrabromide complexes of phenylhydrazones, the N–H stretching bands almost disappear. This indicates that the adduct formation takes place mainly with phenylazo tautomeric form-II.

C=N, N=N and N–N Stretching Frequencies. Weak bands observed in the spectra of the phenylhydrazones in 1620—1652 cm^{-1} region are assigned to ν(C=N).[7-10]

A tautomeric change in phenylhydrazones would be expected to give a new band corresponding to N=N stretching vibration. The specific assignment of the N=N stretching modes in aromatic azo compounds is difficult due to the interference of C=C ring vibrations.[8]

The N–N stretching modes are absent in the titanium tetrachloride and tetrabromide complexes, further supporting the adduct formation with isomer-II. The presence of N–N stretching bands of medium intensity in titanium tetrafluoride complexes supports the existence of the phenylhydrazones mainly in the isomeric form-I in these complexes.

Ti–N and Ti–X Stretching Bands. The new bands occurring in 570—513 cm^{-1} region in the complexes are tentatively assigned to ν(Ti-N).[11,12] The magnitude of the ν(Ti-N) is in good agreement with the thermal stability of complexes.

The occurrence of ν(Ti-X) modes in the octahedral region in the spectra of the complexes shows that they have octahedral geometry.[13,14]

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