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PSEUDO-HALOGEN DERIVATIVES OF MONOSILANE

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Abstract—Silyl *iso*-cyanide, SiH_3NC, and silyl *iso*-thiocyanate, SiH_3NCS, have been prepared and characterized by the measurement of some of their physical properties. Some of the chemical properties of these compounds have also been studied. Unsuccessful attempts to prepare silyl *iso*-cyanate, SiH_3NCO, have been made. Several of the fundamental infra-red absorption bands of silyl *iso*-cyanide and *iso*-thiocyanate have been measured.

In this paper the preparation, properties, and reactions of silyl *iso*-cyanide, SiH_3NC, and silyl *iso*-thiocyanate, SiH_3NCS, are described. These compounds are formally inorganic analogues of methyl *iso*-cyanide and methyl *iso*-thiocyanate, and as such they might have been expected to exhibit somewhat similar properties. However, it has been shown in recent papers(1a–c) that both the physical and chemical properties of most silyl compounds are greatly different from those of their methyl analogues, chiefly because of the ability of silicon to increase its co-ordination number to above 4, and to accept π-bonds from elements of Groups V, VI, and VII. It was the purpose of this research, therefore, to investigate the extent of the difference between analogous silyl and methyl pseudo-halides.

Silyl *iso*-cyanide, SiH_3NC, has been prepared previously(2) from silyl iodide and silver cyanide, but it was reported as silyl cyanide, SiH_3CN. No complete analysis was carried out on the compound and no chemical properties were given. The only physical property reported was a melting-point. No silyl thiocyanate derivatives have so far been described.

Silyl *iso*-cyanide was prepared in yields of over 90 per cent by the action of silyl iodide vapour on silver cyanide at room temperature, viz:

$$SiH_3I + AgNC \rightarrow SiH_3NC + AgI$$

It was also prepared from silyl iodide vapour and mercuric cyanide at slightly elevated temperatures.

The melting-point of silyl *iso*-cyanide was 32·4° (32·3° from the point of intersection of vapour pressure curves of solid and liquid). The higher melting-point, 34°, previously reported for the compound(2) was presumably caused by a too rapid rate of heating. The solid has an extremely high vapour pressure near its melting-point, and an insulating cushion of vapour is readily formed between the solid and the sides of the melting-point tube. The liquid supercooled greatly, and the freezing-point (three determinations) was 24·0–24·1°. For the solid, the vapour pressures in

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(1) (a) Emeléus, MacDiarmid, and Maddock, *J. Inorg. Nucl. Chem.*, **1**, 195, (1955).

(1) (b) Aylett, Emeléus, and Maddock, *J. Inorg. Nucl. Chem.*, **1**, 187, (1955).

(1) (c) Stone and Seyferth, *J. Inorg. Nucl. Chem.*, **1**, 112, (1955).

(2) Emeléus, Maddock, and Reid, *J. Chem. Soc.*, 353, (1941).

the range —20° to 31° were represented by the equation $\log_{10} P = -\frac{2550}{T} + 10{\cdot}951$; the molar heat of sublimation in this range was 11,670 cal/mol, and the calculated vapour pressure at 0·0° was 4·14 cm. For the liquid, the vapour pressures in the range 26° to 46° were represented by the equation $\log_{10} P = -\frac{1567}{T} + 7{\cdot}735$; the molar heat of vaporization in this range was 7169 cal/mol; TROUTON'S Constant was 22·2, and the boiling-point (extrapolated) 49·6 ± 0·3°. Silyl *iso*-cyanide was found to be a colourless solid which readily sublimed *in vacuo* at room temperatures to form long crystals up to 2 cm in length. It was not spontaneously inflammable in air, but burned with a bright yellow flame when ignited. It decomposed very slowly in the dark at room temperatures over a period of one to two years to an extent of about 90 per cent, as indicated by the equation below,

$$2\,x\mathrm{SiH_3NC} \rightarrow x\mathrm{SiH_4} + x\mathrm{HCN} + [\mathrm{SiHCN}]_x.$$

Decomposition was greatly accelerated by traces of mercury. Silyl *iso*-cyanide also decomposed slightly when held near its boiling-point for several hours. It was hydrolysed rapidly and quantitatively by cold water to form disilyl ether according to the equation below,

$$2\mathrm{SiH_3NC} + \mathrm{H_2O} \rightarrow (\mathrm{SiH_3})_2\mathrm{O} + 2\mathrm{HCN}.$$

It did not react at room temperature in the vapour phase with silver chloride to any appreciable extent.

Silyl *iso*-thiocyanate was prepared in 66 per cent yield by the action of silyl iodide vapour on silver thiocyanate at room temperature, viz:—

$$\mathrm{SiH_3I} + \mathrm{AgNCS} \rightarrow \mathrm{SiH_3NCS} + \mathrm{AgI}.$$

The melting-point of silyl *iso*-thiocyanate was —51·8 ± 0·2°. Vapour pressures in the range —33° to 10° were represented by the equation $\log_{10} P = -\frac{1950}{T} + 8{\cdot}340$; the molar heat of vaporization in this range was 8923 cal/mol; TROUTON'S Constant was 25·0; the boiling-point (extrapolated) was 84·0 ± 4°, and the calculated vapour pressure at 0·0° was 1·60 cm. The density at 20·0° was 1·05. Silyl *iso*-thiocyanate was found to be a colourless liquid with a pungent sulphurous acetic-acid-like smell. It slowly decomposed to an extent of 74 per cent during twelve days at room temperature. Hydrogen, monosilane, and an unidentified solid were formed. The *iso*-thiocyanate was not spontaneously inflammable in air, but burned with a blue flame when ignited. It was hydrolysed rapidly by cold water to form disilyl ether. The yield of ether was 46·5 per cent of that calculated from the equation below,

$$2\mathrm{SiH_3NCS} + \mathrm{H_2O} \rightarrow (\mathrm{SiH_3})_2\mathrm{O} + 2\mathrm{HCNS}.$$

An attempt was made to prepare a silyl cyanate by the action of silyl iodide vapour on silver cyanate at room temperature. The desired compound was not obtained, and the reaction proceeded according to the equation below,

$$\mathrm{SiH_3I} + 5\mathrm{AgCNO} \rightarrow \mathrm{Si(NCO)_4} + \mathrm{HOCN} + \mathrm{H_2} + 4\mathrm{Ag} + \mathrm{AgI}.$$

Silyl iodide did not react with potassium cyanate, even after twelve days at room temperature. The action of silyl *iso*-thiocyanate vapour on silver cyanate at room temperature was vigorous, but only $Si(NCO)_4$ and HOCN could be isolated from the reaction products.

It appears highly probable that a replacement or "conversion series" similar to that proposed by Eaborn(3) and extended by Anderson(4) for the preparation of alkyl-substituted silyl derivatives may also exist for unsubstituted silyl compounds. In a previous paper(1a) it was shown that silyl iodide reacted with the appropriate silver salt to form disilyl sulphide or selenide. This fact, together with the methods of preparation of silyl *iso*-cyanide and *iso*-thiocyanate given above, strongly supports such a suggestion.

There is at present insufficient evidence to indicate definitely whether the compounds described in this paper are the normal- or *iso*-derivatives. Hydrolysis cannot be used to distinguish the isomers as with the methyl compounds. The general hydrolysis types are given below,

$$\text{(i)}\ MH_3CH \xrightarrow{H_2O} MH_3CONH_2 \xrightarrow{H_2O} MH_3COONH_4$$

$$\text{(ii)}\ MH_3NC \xrightarrow{H_2O} MH_3NH_2 + HCOOH$$

$$\text{(iii)}\ MH_3CN \xrightarrow{H_2O} MH_3OH + HCN$$

$$\text{(iv)}\ MH_3NC \xrightarrow{H_2O} MH_3OH + HCN$$

followed by $2\ MH_3OH \rightarrow (MH_3)_2O + H_2O$. Both types of hydrolysis can be assumed to take place regardless of whether M is Si or C, but in the case of the methyl compounds reactions (iii) and (iv) are so extremely slow that even the slow reactions (i) and (ii) can take place. However, in the case of silyl compounds, reactions (iii) and (iv) occur almost instantaneously, and consequently there is no time available for the hydrolysis of the CN group while it is still attached to the Si as indicated in equations (i) and (ii). Until there is evidence to the contrary, it seems reasonable to assume that the cyanide is the *iso*-derivative by analogy with the methyl analogue which is formed by the action of methyl iodide on silver cyanide.(5) Both methyl *n*- and *iso*-thiocyanates are asymmetric top molecules,(6) whereas the silyl thiocyanate compound is shown by its infra-red absorption spectrum(7) to be a symmetric top molecule. This implies a linear Si—N—C—S or Si—S—C—N chain, which is more likely for the $Si \underline{\leftarrow} N{=}C{=}S$ structure produced by π-bonding of the N to the silicon. Consequently the compound is probably silyl *iso*-thiocyanate.

The fact that silyl *iso*-thiocyanate is a symmetric top molecule indicates that there must be strong π-bonding between the nitrogen and silicon. This hypothesis is also supported by the fact that liquid silyl *iso*-thiocyanate is considerably associated

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(3) Eaborn, *J. Chem. Soc.*, 3077 (1950).

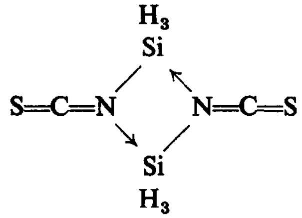
(4) (a) Anderson and Fischer, *J. Org. Chem.*, **19**, 1296, (1954).
(b) Anderson and Vasta, *ibid.*, 1300.

(5) (a) Gauthier, *Ann. Chim. Phys.*, (iv), 222, (1869).
(b) Gauthier, *Annalen*, 152, 222, (1869).

(6) Beard and Dailey, *J. Amer. Chem. Soc.*, **71**, 929, (1949).

(7) MacDiarmid and Maddock, *J. Inorg. Nucl. Chem.*, (in press).

(Trouton's Constant, 25·0). This could be explained by a type of *inter*-molecular bonding as shown below



Infra-red absorption spectra of silyl *iso*-cyanide and *iso*-thiocyanate were prepared. Several of the fundamental absorption bands of both compounds were identified. The spectrum of the *iso*-thiocyanate is discussed in greater detail elsewhere.(7)

EXPERIMENTAL

All experimental work was conducted in an all-glass vacuum system, taps being lubricated with Apiezon grease. When an attack on the tap grease was considered likely, the taps were replaced by glass diaphragms, which could be broken electromagnetically as required. Vapour pressure measurements above room temperature were carried out in an all-glass tensimeter.

Silyl iodide was prepared from silane and hydrogen iodide.(1b)

Before any physical or chemical property of the compound under investigation was studied, the purity of the compound was first checked by measuring its vapour pressure at 0·0°.

PRODUCTION AND REACTIONS OF SILYL *ISO*-CYANIDE

Reaction of Silyl Iodide with Silver Cyanide

The reaction was studied by streaming the vapour of silyl iodide (1·020 g) through a horizontal tube charged with silver cyanide (20 g) and glass wool. The reaction tube became warm and the rate of flow of silyl iodide was controlled to avoid over-heating. A little hydrogen was formed. Unreacted silyl iodide was distilled off from the silyl *iso*-cyanide at −78°, and re-passed through a fresh amount of silver cyanide. A total of 0·9270 g of silyl *iso*-cyanide was obtained. The material (0·1401 g) was analysed by hydrolysis with 30 per cent sodium hydroxide solution. Hydrogen evolved was measured. The cyanide in the hydrolysate was determined by Liebeg's method.(8) Silicon was determined by hydrolysing another sample (0·1129 g), acidifying the hydrolysate strongly with hydrochloric acid, and weighing as silica. (Found: H 5·24, Si 49·5, CN 45·2, per cent M 57·5 SiH_3NC requires H 5·26, Si 49·1, CN 45·6, per cent M 57·0).

Reaction of Silyl Iodide with Mercuric Cyanide

The reaction was studied as in the previous experiment, using 0·7 g of silyl iodide and 12 g of mercuric cyanide. No reaction took place at room temperature, but when the reaction tube was warmed gently with a smoky coal-gas flame, reaction ensued. No hydrogen was evolved. Silyl *iso*-cyanide was found to be present in the middle fraction to distil from a bath at −46°. It was identified by its distillation properties and by its melting point (33°).

Decomposition of Silyl iso-Cyanide

Small amounts (0·06 to 0·1 g) of silyl *iso*-cyanide were sealed in small tubes *in vacuo*. Large amounts of solid phase were present. Some samples showed a faint black band of condensed mercury vapour. The pure samples remained colourless for approximately six months, and then a dark brown solid film began to form evenly over the entire inside surface of the tubes. The mercury-contaminated samples decomposed much more rapidly. No hydrogen was found to be present after opening a tube of absolutely pure silyl *iso*-cyanide after a period of twenty months. Substances present were unchanged silyl *iso*-cyanide (0·0112 g; M (found) 58·2, (calcd.) 57·0; vapour pressure at 0·0° (found)

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(8) Vogel, *Quantitative Inorganic Analysis*, Longmans, Green & Co., London, 1946, page 327.

4·23 cm, (calcd.) 4·14 cm), silane (0·0264 g; *M* (found) 32·1, (calcd.) 32·0), and a non-volatile brown solid which gave off much hydrogen on hydrolysis with aqueous alkali (Si—H and/or Si—Si bonds present). The hydrolysate gave very strong tests for cyanide ion.

Hydrolysis of Silyl iso-*Cyanide*

Silyl *iso*-cyanide (0·1370 g) was distilled into an evacuated tube immersed in liquid nitrogen together with 0·5 ml of degassed distilled water. The tube was sealed off and was allowed to warm up to room temperature. Reaction occurred instantaneously, and after five minutes the tube was opened, and volatile material removed. No hydrogen was present and no residue remained in the tube. The products other than unchanged water were, disilyl ether (0·0940 g; M (found) 78·2, (calcd.) 78·0; Vapour pressures (found) 6·27 cm at −64·0°, 9·39 cm at −57·8°, 11·1 cm at −55·0°. Literature values(9) are 5·8 cm at −65°, 8·1 cm at −60°, 10·9 cm at −55°), and hydrogen cyanide (0·0650 g; M (found) 27·2, (calcd.) 27·0; Vapour pressure at 0·0° (found) 26·25 cm. Literature value(10) at −0·1° is 26·4 cm). The yields of both the disilyl ether and hydrogen cyanide were 100·2 per cent of the theoretical.

Reaction of Silyl iso-*Cyanide with Silver Chloride*

The reaction was studied by streaming the vapour of silyl *iso*-cyanide (0·2246 g) through a horizontal tube charged with silver chloride (15 g) and glass wool. The *iso*-cyanide was passed through the tube twice. No reaction appeared to occur. Substances recovered from the reaction were silyl *iso*-cyanide (0·2157 g; vapour pressure at 0·0° (found) 4·21 cm, (calcd.) 4·14 cm), which corresponded to a 90 per cent recovery, and an unidentified material (0·0058 g) which had distillation properties consistent with silyl chloride, SiH_3Cl, but which could not be identified further because of the very small amount of material available.

PRODUCTION AND REACTIONS OF SILYL *ISO*-THIOCYANATE

Reaction of Silyl Iodide with Silver Thiocyanate

The silver thiocyanate was formed by precipitation from silver nitrate and potassium thiocyanate. The reaction was studied by streaming the vapour of silyl iodide (1·1560 g) through a horizontal tube charged with silver thiocyanate (20 g) and glass wool. The reaction proceeded extremely vigorously, with the evolution of much heat and hydrogen if the rate of passage of the silyl iodide was too great: consequently the rate of flow of silyl iodide was controlled to avoid over-heating and decomposition. Silyl *iso*-thiocyanate (0·4340 g) was found to be present amongst the products of the reaction in a fraction which condensed in a trap at −64°. Small amounts of thiocyanic acid were also formed and passed through the −64° trap, and then immediately polymerized on warming to room temperature. The silyl *iso*-thiocyanate (0·1152 g) was analysed by hydrolysis with 30 per cent sodium hydroxide solution. Hydrogen evolved was measured. The thiocyanate in the hydrolysate was determined by the addition of excess standard silver nitrate solution followed by back titration with standard potassium thiocyanate. Silicon was determined by hydrolysing another sample (0·1564 g), acidifying the hydrolysate strongly with hydrochloric acid, and weighing as silica. (Found: H 3·36, Si 31·35, CNS 65·1, per cent *M* 89·5. SiH_3NCS requires H 3·37, Si 31·45, CNS 65·2; per cent M 89·0).

Decomposition of Silyl iso-*Thiocyanate*

Silyl *iso*-thiocyanate (0·1214 g) was sealed in a 12-ml tube *in vacuo* and was stored for twelve days at room temperature. A large liquid phase was present at all times. When the tube was opened, 2·4 cc hydrogen at N.T.P. were present. This was equivalent to 7·1 per cent of the hydrogen in that portion of the sample which had decomposed. Substances recovered were unchanged silyl *iso*-thiocyanate (0·0316 g or 26 per cent recovery; M (found) 89·9, (calcd.) 89·0; Vapour pressure at 0·0° (found) 1·63 cm, (calcd.) 1·60 cm), and monosilane (0·0011 g; M (found) 28·5, (calcd.) 32·0); the latter compound gave no test for sulphide ions on hydrolysis, and was not, therefore, hydrogen sulphide. Small amounts of two high-boiling-point unidentifiable liquids were also obtained. A

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(9) Stock, Somieski, and Wintgen, *Ber.*, **50**, 1754, (1917).

(10) Perry and Porter, *J. Amer. Chem. Soc.*, **48**, 299, (1926).

white solid which was not sulphur remained in the storage tube. It dissolved in potassium hydroxide solution with little evolution of hydrogen. The solution gave strong reactions to tests for thiocyanate and cyanide ions. Therefore it appears that the solid was probably complex polymerized thiocyanic acid derivatives.

Hydrolysis of Silyl iso-*Thiocyanate*

Silyl *iso*-thiocyanate (0·1238 g) was distilled into an evacuated tube immersed in liquid nitrogen together with 0·5 ml of degassed distilled water. The tube was sealed off and allowed to warm up to room temperature. Reaction occurred as soon as the compound began to melt, and appeared to be complete by the time it had reached room temperature. After five to ten minutes the tube was opened, and 16·9 cc of hydrogen at N.T.P. were found to be present. The volatile material was removed, and a white powder remained in the hydrolysis vessel. The products, other than unchanged water, were disilyl ether (0·0252 g; M (found) 77·5, (calcd.) 78·0; vapour pressures (found) 5·77 cm at −64·5°, 8·78 cm at −58·0°. Literature values$^{(10)}$ are 5·8 cm at −65°, 8·1 cm at −60°, 10·9 cm at −55°), and thiocyanic acid (0·0142 g; M (found) 54·0, (calcd.) 59·0). The latter compound was also identified by the fact that it decomposed especially in the presence of water to give xanthine hydride, the white solid remaining in the hydrolysis vessel, and hydrogen cyanide.$^{(11)}$ The traces of hydrogen cyanide present would account for the lowering of the molecular weight of the thiocyanic acid from which it could not be separated by distillation. The yield of disilyl ether was 46·5 per cent of the theoretical.

Reaction between Silyl iso-*Thiocyanate and Silver Cyanate*

See next section.

ATTEMPTED PREPARATIONS OF SILYL CYANATE

Reaction between Silyl Iodide and Silver Cyanate

Silver cyanate was prepared by precipitation from silver nitrate and potassium cyanate. The reaction was studied by streaming the vapour of silyl iodide (0·3902 g) through a horizontal tube charged with silver cyanate (15 g) and glass wool. The reaction tube became warm and the rate of flow of silyl iodide was controlled to avoid over-heating. A little hydrogen was formed. The products isolated were cyanic acid (0·15 g; M (found) 43·0, (calcd.) 43·0; boiling-point (found) 24·0°. Literature value$^{(12)}$ is 23·6°), and silicon tetra-*iso*-cyanate (0·40 g; melting-point (found) 26·0–26·3°. Literature value$^{(13)}$ is 26 ± 0·5°). The identity of the latter compound was checked by hydrolysing it in aqueous alkali. No hydrogen was evolved (indicating the absence of Si—H or Si—Si bonds) and the hydrolysate gave excellent qualitative tests for the cyanate ion. The contents of the reaction tube had changed to a deep black colour, indicating the probable presence of finely-divided metallic silver.

The Reaction between Silyl Iodide and Potassium Cyanate

The reaction was studied by placing silyl iodide (0·5235 g) and potassium cyanate (0·25 g) in a 250-ml reaction vessel, which was sealed and left at room temperature for twelve days. Some liquid silyl iodide was present at all times. No hydrogen was evolved, and an almost quantitative recovery of silyl iodide (*M* (found) 156·0, (calcd.) 158·0) was obtained.

Reaction between Silyl iso-*Thiocyanate and Silver Cyanate*

The reaction was studied by streaming the vapour of silyl *iso*-thiocyanate (0·1434 g) through a horizontal tube charged with silver cyanate (15 g) and glass wool. The reaction tube became warm and the rate of flow was controlled to avoid over-heating. A little hydrogen was evolved. The substances isolated were cyanic acid (0·0445 g; M (found) 44·3, (calcd.) 43·0; boiling-point (found) 21·3°, Literature value$^{(12)}$ is 23·6°), and silicon tetra-*iso*-cyanate (0·0762 g); the identity of the latter compound was gained from its distillation properties in the vacuum system, and from the fact that, when it was hydrolysed in aqueous alkali, very little hydrogen was evolved (indicating the absence of Si—H and/or Si—Si bonds). The hydrolysate gave strong tests for cyanate ion. An unidentified compound

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(11) LINNARD, *Z. anorg. Chem.*, **236**, 200, (1938).

(12) FORBES and ANDERSON, *J. Amer. Chem. Soc.*, **62**, 761, (1940).

(13) WILLIAMS, *Cyanogen Compounds*. Edward Arnold & Co., London, 1948, page 308.

(0·1016 g; *M* 44·6), which passed through a −134° bath, was also obtained. When hydrolysed, hydrogen was evolved (indicating the presence of Si—H bonds), and the hydrolysate gave no positive test for sulphide ions.

INFRA-RED ABSORPTION SPECTRA

A Perkin-Elmer model 21 double-beam recording I-R spectrophotometer with a sodium chloride optical system was used. "Glyptal" cement was used to hold the 5-mm sodium chloride end-plates in position on the 10-cm gas cell.

With silyl *iso*-cyanide, pressures of 8·67 cm, 1·00 cm, and 0·13 cm were used. Measurements on silyl *iso*-thiocyanate were carried out at pressures of 3·18 cm, 0·5 cm, and 0·075 cm. During the measurement at the highest pressure a minute amount of hydrogen was formed.

The silyl *iso*-cyanide spectrum indicates that the compound is of the symmetric top type. Silyl *iso*-thiocyanate is also a symmetric top molecule, and is discussed more fully in another paper.(7) Several of the fundamental absorption bands of both compounds are listed below:

Vibration	SiH_3NC cm^{-1}	SiH_3NCS cm^{-1}
Si—H stretch	2208 (s) overtone 1613 (w) overtone 1890 (w) overtone 3125 (m)	2198 (s) overtone 1905 (m) overtone 3145 (w)
SiH_3 deformation (i.e., SiH_3 bend)	914 (s); 923 (s); 929 (s) Probable overtone 1351 (m) Probable overtone 1370 (m)	946 (s); 952 (s) Probable overtone 1414 (m) Probable overtone 1420 (m)
SiH_3 rock + unidentified bands	691 (s) 689 (s) Broad bands	696 (s) 721 (s) Broad bands—possibly with CS or CN vibration
NCS stretch(14, 15)		2045 (s); 2096 (s)
Unidentified	1166 (w) 2033 (w) 2433 (w)	1031 (s) 1038 (s) 1094 (m) possibly disilyl ether impurity 1661 (w) 2538 (m) 2597 (s) 2646 (m) 3521 (w) 4082 (w)

w = weak m = moderate s = strong

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(14) Gordy and Williams, *J. Chem. Phys.*, **4**, 85, (1936).
(15) Kahovec and Kohlrausch. *Z. phys. Chem.*, **B37**, 421, (1937).