Contribution from the Department of Chemistry
of Texas A. & M. University, College Station, Texas

Arsine Selenides: The Fundamental Arsenic–Selenium Vibration

By RALPH A. ZINGARO and ASPET MERIJANIAN

Received October 7, 1963

Nine arsine selenides have been prepared and characterized. We have been unable to prepare triphenylarsine selenide as a stable compound. The fundamental As–Se vibration occurs as a doublet in these molecules, but an unequivocal explanation for this splitting awaits further experimentation.

Introduction

As part of an over-all program concerned with the synthesis of group V chalcogenides and studies of their physical properties, we have characterized nine trialkylarsine selenides. Also, we have observed the infrared absorption of these molecules in the cesium bromide region and have located the fundamental As–Se stretching frequency.

Trimethylarsine selenide was prepared by Renshaw and Holm[1] by the direct reaction of elemental selenium with impure trimethylarsine. We have been able to reproduce their results and observations. The formation of triphenylarsine selenide as an intermediate during the reaction of selenium dioxide with triphenylarsine[2] has been suggested, but the compound was apparently not isolated since neither analytical data nor a melting point were reported. We have attempted the preparation of triphenylarsine selenide by various methods without success.

Experimental

Trimethylarsine.—This compound was prepared in 63% yield by the reaction of arsenic trichloride with methylmagnesium iodide in *n*-butyl ether. The details and advantages of carrying out the preparation in this manner are described elsewhere[3] for trimethylphosphine. This method involves the thermal decomposition of the trimethylarsine–magnesium halide adduct. A temperature of 125° was found to be adequate to bring about essentially quantitative decomposition into the arsine.

Tris(*n*-octyl)arsine.—This compound was prepared in the usual manner by the reaction of arsenic trichloride with *n*-octylmagnesium chloride in ethyl ether. The pure compound is a colorless liquid, b.p. 167° (0.04 mm.), refractive index at 32°, 1.4956.

Anal. Calcd. for $C_{24}H_{51}As$: C, 69.55; H, 12.39; As, 18.07. Found: C, 69.70; H, 12.55; As, 18.09.

Mixed Arsines.—In those cases where the arsine was of the formula RR'_2As, the alkyldichloroarsine, $RAsCl_2$, was prepared by reduction of the alkylarsonic acid, $RAs(O)(OH)_2$, in concentrated hydrochloric acid with sulfur dioxide using potassium iodide as a catalyst. The alkyldihaloarsine was extracted with ether, dried, and vacuum distilled. The alkyldihaloarsines are *very hazardous compounds* and extreme *care should be exercised* to avoid breathing of the fumes or contacting the liquids with the skin.

Other Arsines.—All of the other arsines are well characterized in the literature. They were prepared by the condensation of arsenic trichloride, or of the alkyldichloroarsine, with the appropriate Grignard reagent or *n*-butyllithium. The preparation and purification of the arsine selenide is greatly simplified and the yield substantially increased if the pure, freshly redistilled arsine is used in its preparation.

Arsine Selenides.—The arsine selenides were prepared by refluxing the arsine with an equivalent or slight excess of selenium powder under nitrogen for 2–3 hr. When the selenide is a solid, it is preferable to use ethanol as a solvent, although benzene is quite satisfactory. Following reflux, the mixture is filtered to remove unreacted selenium and the filtrate is evaporated until crystallization begins. If crystallization does not occur, or if the selenide is a liquid, the entire amount of solvent is removed under reduced pressure. The impure crystalline solids can then be recrystallized from the appropriate solvents listed as footnotes in Table I.

When the product was a liquid at room temperature, the most satisfactory method of purification was to dissolve the impure product in the minimum volume of petroleum ether, ethyl ether, or a mixture of both, so as to form a homogeneous solution. The solution was cooled in a Dry Ice–acetone mixture to freeze out the selenide. The filtrate was decanted and the process repeated until a reproducible freezing point or refractive index was obtained. The liquids were yellow or pale amber in color.

A typical example of the preparation of a trialkylarsine selenide is as follows. A 6.2-g. (0.03 mole) sample of freshly distilled tris(*n*-propyl)arsine was refluxed with 2.3 g. (0.03 mole) of finely powdered selenium in 100 ml. of ethanol under an atmosphere of nitrogen. The selenium was slowly taken up and after 4 hr. the hot solution was filtered through a medium porosity sintered glass filter in order to remove unreacted selenium. The solution was evaporated under reduced pressure almost to dryness in order to isolate the crystalline compound. The product was very soluble in ethanol, acetonitrile, and benzene. It was recrystallized from a mixture containing equal volumes of low boiling petroleum ether and ethyl ether to a reproducible melting point of 48°. The pure product was obtained in the form of colorless needles weighing 3.5 g. (43% yield), which very slowly deposited selenium on standing.

Attempted Preparation of Triphenylarsine Selenide.—Reference has been made[2] to the reaction of triphenylarsine with selenium dioxide to form triphenylarsine oxide and triphenylarsine selenide. Accordingly, 15 g. (0.05 mole) of triphenylarsine and 1.85 g. (0.0165 mole) of selenium dioxide were dissolved in 100 ml. of dry benzene. A homogeneous solution was formed which was allowed to stand for 48 hr. Elemental selenium and white needles identified as triphenylarsine were separated. The benzene was evaporated under reduced pressure and the crystalline solids which separated were collected. Approximately 12 g. or 80% of the original arsine was recovered unreacted. Following recrystallization from benzene and alcohol, one fraction of crystals was identified by melting point and mixture melting point as triphenylarsine oxide. The total yield of this compound was 1 g. and this corresponds to somewhat less than 10% conversion to the oxide. About 0.9 g. of elemental selenium was recovered, which is 70% of that theoretically obtainable from the original quantity of SeO_2. There was no evidence of any triphenylarsine selenide formation. The preceding experiment was repeated

---

[1] R. R. Renshaw and G. E. Holm, *J. Am. Chem. Soc.*, **42**, 1471 (1920).

[2] N. N. Mel'nikov and M. S. Rokitskaya, *J. Gen. Chem. USSR*, **8**, 834 (1938); *Chem. Abstr.*, **33**, 1267^5 (1939).

[3] R. A. Zingaro and R. E. McGlothlin, *J. Chem. Eng. Data*, **8**, 226 (1963).

TABLE I

ARSINE SELENIDES R_3AsSe

R_3	Analyses C Calcd.	Analyses C Found	Analyses H Calcd.	Analyses H Found	Analyses As Calcd.	Analyses As Found	M.p., °C.	Mol. wt. in C_6H_6 Calcd.	Mol. wt. in C_6H_6 Found	Refractive index
$(CH_3)_3$[a]							Dec. 100	199	214	
$(C_2H_5)_3$[b]	29.88	29.85	6.27	6.08			129–130	241	238	
$(n\text{-}C_3H_7)_3$[c]	38.17	38.19	7.47	7.59			48	283	283	
$(n\text{-}C_4H_9)_3$[d]	44.31	44.25	8.37	8.29			13			1.5387 (26°)
$(n\text{-}C_4H_9)(CH_3)_2$[e]	29.89	29.90	6.27	6.12			84–85			
$(n\text{-}C_4H_9)_2CH_3$[f]	38.18	38.06	7.48	7.38			24–25			
$CH_3(C_2H_5)_2$[g]	26.45	26.43	5.77	5.59			82–83	227	235	
$(n\text{-Octyl})_3$[d]	58.40	58.61	10.42	10.42	15.18	15.05	(−5)–(−4)	493.5	494	1.5048 (32°)
		58.85		10.26		15.52			494	
$(\text{Cyclohexyl})_3$[h]	53.62	53.91	8.22	8.57	18.57	18.81	183	399	415	

[a] This compound was not analyzed. Its physical properties paralleled those reported by Renshaw and Holm, ref. 1. [b] Recrystallized from 95% ethanol. [c] Recrystallized from ethyl ether–petroleum ether mixture. [d] Frozen out of low boiling petroleum ether at Dry Ice–acetone temperature. [e] Recrystallized from ethanol–water mixture. [f] Frozen out of ethyl ether at Dry Ice temperature. [g] Recrystallized from ethanol–acetone mixture. [h] Recrystallized from benzene–ethanol mixture.

with refluxing, but again no evidence of selenide formation was noted.

In further attempts to prepare this compound, direct combination of the arsine with elemental selenium by fusion in a sealed tube at 225° or refluxing in various solvents all led to quantitative recovery of the unreacted substances.

The reaction of gaseous hydrogen selenide with triphenylarsine dichloride or dibromide was also attempted. Although the hydrogen halides formed, triphenylarsine and elemental selenium were the only products isolated.

Reaction of Arsine Selenides with Iodine.—Inasmuch as phosphine sulfides and selenides form well-defined crystalline complexes with halogens,[4] the possible formation of such compounds with the arsine selenides was also investigated. The techniques used in attempting the preparation of these compounds paralleled those previously described.[4] Iodine-bearing compounds formed rapidly as crystalline precipitates varying from tan to brown to maroon in color, but in no case were stoichiometrically pure materials isolated. These materials could be redissolved and recrystallized, but all attempts to obtain material of reproducible composition were unsuccessful. Every indication was that nonstoichiometric halogen addition compounds were formed.

Infrared Spectra.—All spectra were recorded on a Perkin-Elmer Model 21 spectrometer equipped with CsBr optics. For spectra run at various temperatures a heated cell with CsI windows manufactured by the Limit Research Corp., Darien, Conn., was employed. The temperature was measured by means of a thermocouple and read off a standard potentiometer.

Results and Discussion

The arsine selenides that were prepared, along with pertinent physical data, are listed in Table I. The compounds are relatively stable under ordinary atmospheric conditions although the separation of elemental selenium takes place slowly in all cases. Recrystallization of the crystalline solids is not difficult and any gray selenium can be removed by filtration. The removal of colloidal red selenium is greatly facilitated by the addition of benzene to the solvent used for purification.

Our inability to prepare the triphenylarsine selenide probably is due to the inherent instability of this particular molecule. All of the methods of preparation investigated resulted in the recovery of unreacted triphenylarsine, or in the formation of triphenylarsine from the starting products. The reaction of triphenylarsine dichloride with hydrogen selenide corresponds to the stoichiometry

$$(C_6H_5)_3AsCl_2 + H_2Se \longrightarrow 2HCl + (C_6H_5)_3As + Se$$

The formation of highly crystalline addition compounds with iodine without the loss of selenium is interesting, especially in view of the fact that arsine sulfides[4] react with iodine with the loss of sulfur to form trialkyliodoarsonium triiodides. The addition compounds which are formed when arsine selenides react with iodine appear to be completely nonstoichiometric. The preparation of stoichiometric halogen addition compounds may be possible under the proper conditions. Further investigation of these compounds is planned. In connection with the donor ability of these molecules, it should be added that in all attempts to prepare crystalline complexes with a variety of ions including all of the first series transition metal ions, the crystalline selenide and the transition metal salt were recovered unreacted. However, complex formation in solution was certainly indicated by the color changes which were observed. A general study of the coordination chemistry involving arsine selenides as donor molecules should be both interesting and fruitful.

The infrared absorbance of the arsine selenides in the 540–640 cm.$^{-1}$ range, which is the region of the symmetric and asymmetric As–C stretching vibrations, parallels that observed for the arsine sulfides[5] and will not be discussed further.

The force constant of an As–Se bond can be estimated from Gordy's rule,[6] which gives a value of 6.3 and 3.1 $\times 10^5$ dynes/cm. for a "pure" As–Se double bond and single bond, respectively. These values, when inserted into the fundamental equation for a harmonic oscillator along with the reduced mass, give an upper limit of 520 cm.$^{-1}$ and a lower limit of 372 cm.$^{-1}$ for an isolated As–Se vibration. In Table II are listed the frequencies experimentally observed for this vibration in all of the arsine selenides which were prepared. In every case the spectrum of the parent arsine was also

---

[4] R. A. Zingaro and E. A. Myers, *Inorg. Chem.*, **1**, 171 (1962).

[5] R. A. Zingaro, R. E. McGlothlin, and R. M. Hedges, *Trans. Faraday Soc.*, **59**, 798 (1963).

[6] W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946).

TABLE II

THE FUNDAMENTAL As–Se STRETCHING VIBRATION

Arsine selenide derivative	Physical state	$\tilde{\nu}_{\text{As-Se}}$, cm.$^{-1}$		Separation, $\Delta\tilde{\nu}$	Intensity ratio of doublet[b]
(1) Trimethyl	*a*	336.4			
(2) Triethyl	*a*	332.1	358.3	26.2	1.04
(3) Diethylmethyl	*a*	336.8	346.7	10.8	1.13
(4) Dimethyl-*n*-butyl	*a*	336.8	347.6[c]	10.8	1.41
(5) Di-*n*-butylmethyl	*a*	337.8	347.7[c]	9.9	1.13
(6) Tri-*n*-propyl	Solid	343.6	356.5	12.9	1.09
	a	348.9	357.1	8.2	1.00
(7) Tri-*n*-butyl	*a*	338.4	347.2	8.8	0.98
(8) Tri-*n*-octyl	Pure liquid	331.1	356.4[c]	23.3	1.14
	a	338.9	359.5[c]	20.6	1.18
(9) Tricyclohexyl	*a*	360.4			

[a] Benzene solution, *ca.* 10%. [b] In all cases this is the ratio of the absorbance at the lower frequency to that at the higher frequency. [c] Shoulder, well defined.

observed. The arsines were found to be transparent in the region of the As–Se vibration. The fact that the vibration occurs below the lower limit calculated from the force constants estimated by the use of Gordy's rule is due either to the inherent limitations imposed by the form of the equation, or by the inadequacies in the numerical values required, *viz.*, the bond distances and electronegativities. Qualitatively, however, a low bond order is indicated and the arsenic–selenium bond, at least in these compounds, may well approach the classical covalent type with the more electronegative selenium atom coordinated to arsenic *via* the 4s electron pair of the arsenic atom. The relatively low frequency at which this vibration is found also suggests that there is no contribution resulting from back donation of electrons by either atom.

It will be noted from Table II that with the exception of the trimethyl and tricyclohexyl derivatives, all of the vibrations are observed as doublets. Even when the splitting was relatively narrow, the doublet was always easily resolved. With the exception of the dimethyl-*n*-butyl derivative [Table II (4)], the intensity of the doublet bands was approximately equal, at least within the accuracy attainable by the instrument. The separation between the bands is generally of the order of 10 cm.$^{-1}$, although it is as large as 26 cm.$^{-1}$ in the case of the triethyl derivative.

In an effort to obtain additional information to aid in understanding the origin of this doublet, we observed the behavior of this vibration from room temperature up to 150° for the triethyl-, tripropyl-, trioctyl-, and tricyclohexylarsine selenides. The following general observations were made. There is no significant change, at least within the accuracy of which this instrument is capable, in going from pure liquid to solution [Table II (8)], in going from solid to liquid [Fig. 1 and Table II (6)], or in the actual location of the absorption bands. Also, both the relative intensity and actual location of the bands are temperature independent from room temperature up to 150°. The only obvious change which takes place as the temperature is raised is a decrease in absorption which can be partially attributed to a lowering of the density of the solution with a concurrent decrease in concentration. The decrease in absorption is too large to be attributed solely to such changes and the emission of radiation by the sample and cell at the higher temperature may be a contributing factor.

The possibility of intermolecular association and the existence of an equilibrium between the monomer and associated molecules is ruled out both on the basis of molecular weight determinations (Table I) and the absence of temperature effects. A temperature increase would favor enhancement of the absorption due to the monomer and a concurrent decrease in the absorption due to the associated molecules. Such behavior is not observed. Coupling with a low-frequency mode of about 10 to 26 cm.$^{-1}$ would give rise to a number of difference bands as well as summation bands and the fundamental would surely be of much greater intensity. This possibility, therefore, must also be ruled out.

Another possibility would be the existence of chemical isomers such as R_3AsSe and R_2AsSeR. We believe this to be highly unlikely. Also, we may be dealing with completely separate vibrations, but the actual frequencies of the absorptions in addition to the fact that a singlet is observed for two of the molecules tends to minimize such an argument.

An alternate explanation is based upon the possible existence of modified tetrahedral forms suggested by Bell, *et al.*,[7] to explain the splitting of the P=O stretching frequency in triaromatic esters of phosphorus acids. An examination of molecular models of trialkylarsine selenides shows that at normal tetrahedral bond angles there exists, except in the case of the trimethyl compound, considerable steric hindrance of the alkyl groups. Borrowing the suggestion of Bell, *et al.*, the existence of two stable distortions, each differing in bond angles and bond lengths, is plausible. A separate fundamental As–Se vibration would characterize each of the two forms. The methyl groups are not sterically hindered and presumably would form normal tetrahedral bonds, a single stable form, and the As–Se vibration would be observed as a singlet, as observed. This explanation would also require that in the case of

---

(7) J. V. Bell, J. Heisler, H. Tannenbaum, and J. Goldenson, *J. Am. Chem. Soc.*, **76**, 5185 (1954).

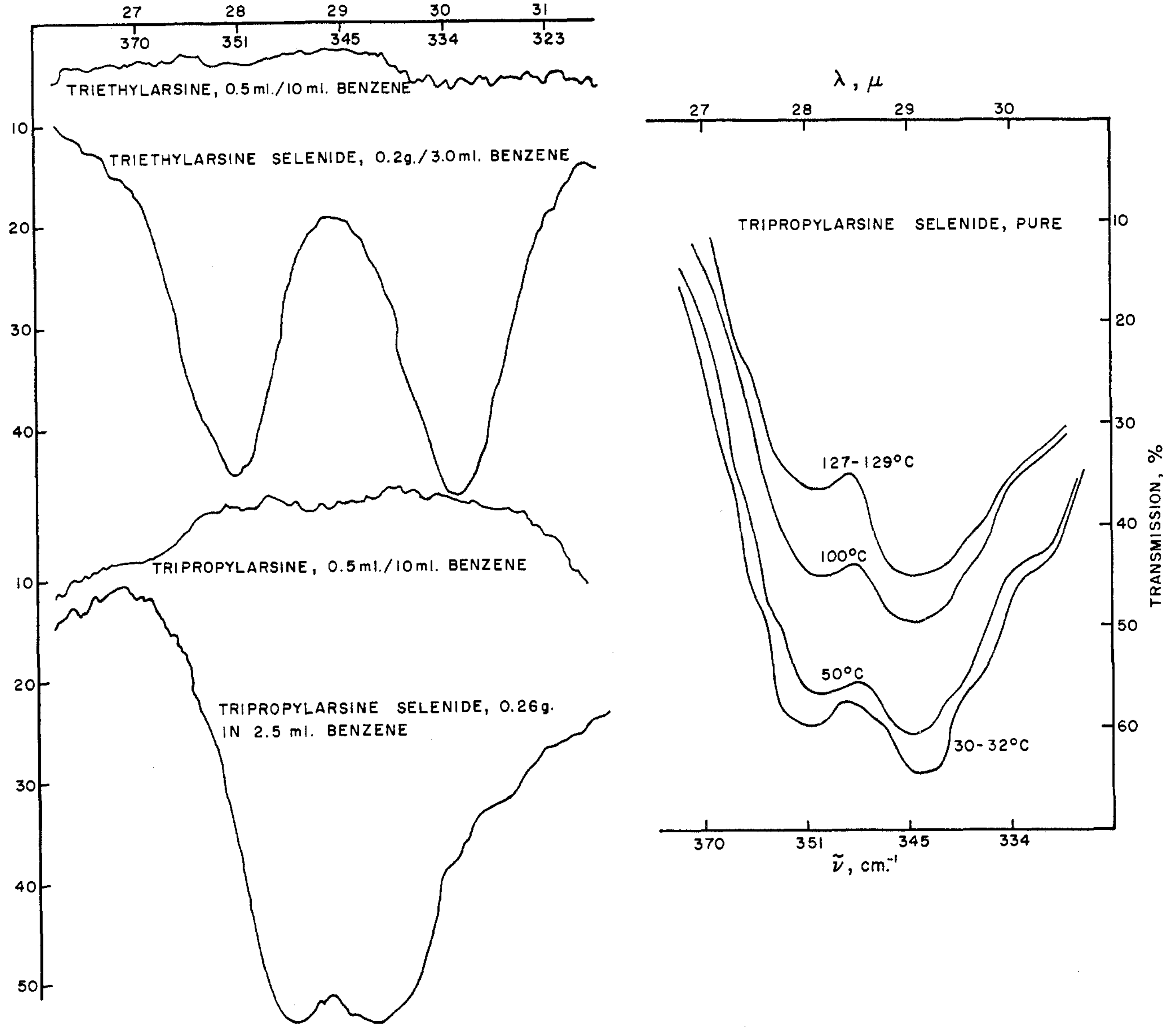

Fig. 1.—Absorption bands due to fundamental As–Se vibration in some arsine selenides.

the tricyclohexyl derivative, for which the vibration is observed as a singlet, only a single configuration is stable.

Since the experimental evidence indicates very strongly that we are dealing with a single molecular form, the most likely suggestion is that the As–Se stretching vibration is in Fermi resonance with the overtone of some lower frequency vibration. This would yield two absorptions of equal or of approximately equal intensity. Confirmation by observation of the missing fundamental may be experimentally difficult. This explanation also suffers from the failure to observe any splitting of the As–Se vibration for the trimethyl and tricyclohexyl compounds. These molecules would certainly be expected to exhibit symmetry requirements identical with those of similar molecules for which splitting was observed.

The foregoing explanations must be considered tentative and additional work in this area, including low temperature observations, is planned in order to explain this very interesting observation.

Inasmuch as the As–Se vibration in the trialkylarsine selenides is experimentally well established, it is worthwhile to estimate the force constant from the fundamental equation for a harmonic oscillator, *viz.*

$$k = (\tilde{\nu}/1307)^2\mu$$

Since the range over which this frequency is located is quite narrow throughout the entire range of aliphatics from trimethyl, total mass 45, $\tilde{\nu}_{\text{As-Se}} = 336.4$, through tricyclohexyl, total mass 249, $\tilde{\nu}_{\text{As-Se}} = 360.4$, the As–Se vibration appears to behave very much as a characteristic group vibration. The value of the reduced mass, μ, will be taken for the atom pair, As–Se. Using an average value of $\tilde{\nu}_{\text{As-Se}} = 348$ cm.$^{-1}$ gives $k_{\text{As-Se}} = 2.7 \times 10^5$ dynes/cm.

Acknowledgment.—This is part of an over-all program of research which is receiving support from the United States Atomic Energy Commission under Contract AT-(40-1)-2733, the Robert A. Welch Foundation, Houston, Texas, and the Selenium and Tellurium

Development Committee. We are indebted to the Shell Oil Company, Deer Park, Texas, for making available to us the use of their infrared equipment. Also we want to thank the Vineland Chemical Company, Vineland, New Jersey, for gifts of various alkylarsonic acids.

Contribution from the Department of Chemistry,
Princeton University, Princeton, New Jersey

Infrared Spectroscopic Study of Isonitrile Derivatives of the Iron Carbonyl Halides

By R. Craig Taylor and W. D. Horrocks, Jr.

Received September 3, 1963

The complexes $Fe(CO)_{4-n}(CNR)_nX_2$, where $n = 0$–4, R = *p*-tolyl or *t*-butyl, and X = Cl, Br, or I, were prepared and the infrared spectra studied in the carbonyl and isonitrile stretching regions. The π-electron accepting abilities of the coordinated carbonyl and isonitrile groups are discussed. Structures of a number of these compounds are postulated on the basis of the number and intensity of the observed infrared bands. Spectral shifts in a series of compounds are found to correlate well with the electronegativities of the halogens.

Introduction

Continuing infrared spectroscopic study of derivatives of transition metal carbonyls, we have investigated the isonitrile derivatives of the iron tetracarbonyl dihalides. Although a number of derivatives of these carbonyl halides have been reported previously,[1–4] a systematic study of these compounds in the carbonyl stretching region has not been made. The replacement of carbonyl groups by isonitrile ligands enables us to study the N–C stretching frequencies in these derivatives. Thus we are able to study the π-electron accepting abilities of both ligands in this series of complexes.

Previous infrared studies[5–9] on mixed isonitrile–carbonyl complexes have indicated that the carbonyl group is a better π-electron acceptor than the isonitrile group. Hence, when both are present, the C–O group bears the greater burden of charge removal from the central metal atom. In carbonyl complexes in which the central metal atom is in a low valence state, for example, the group VI carbonyls, the buildup of negative charge on the metal atom can be relieved by π-electron donation from the metal to the empty π-antibonding orbitals on the carbon monoxide ligand. This lowers the bond order of the C–O bond, thereby lowering the C–O stretching frequency. As the charge on the metal atom is increased in the series Cr^0, Mn^+, Fe^{+2}, the amount of π-electron donation from metal to the carbonyl group decreases, thus increasing the C–O bond order and the resulting C–O stretching frequency.[10]

As shown by a study of Cotton and Zingales,[8] isonitrile molecules being formally isoelectronic with carbon monoxide may function both as σ-donors and π-electron acceptors. Their σ-donor ability is greater than that of carbon monoxide, and this ability is enhanced in complexes with metals in high oxidation states. The π-electron accepting ability of isonitrile ligands is exhibited to a degree in complexes with metals in low or negative oxidation states, but their ability to remove charge is always inferior to that of carbon monoxide. Our results confirm this hypothesis.

We were also able to correlate the inductive effect of the halogens due to their varying electronegativities with the observed infrared spectral shifts.

Experimental

Materials.—The iron tetracarbonyl dihalides were prepared according to the procedures of Hieber and Bader.[11] $Fe(CO)_4Br_2$ and $Fe(CO)_4I_2$ were purified by sublimation. $Fe(CO)_4Br_2$ sublimes readily at 40–45° (1–5 mm.) to give long reddish brown needles. $Fe(CO)_4I_2$ sublimes at 65–70° (5 mm.) to give long brownish black needles. $Fe(CO)_4Cl_2$ could not be sublimed without considerable decomposition. All three complexes were stored in darkened bottles, at −25°. Even at this temperature, $Fe(CO)_4Cl_2$ decomposes slowly.

t-Butyl and *p*-tolyl isonitriles were prepared according to the procedure of Ugi and Meyr.[12]

t-Butylisonitrileiron tetracarbonyl and di-(*t*-butylisonitrile)-iron tricarbonyl were prepared according to the procedures of Cotton and Parish.[7]

Although the *p*-tolylisonitrileiron tetracarbonyl and di-(*p*-tolylisonitrile)iron tricarbonyl complexes are new, they were prepared by a method similar to that of Hieber and von Pigenot.[13] This procedure is described below.

***p*-Tolylisonitrileiron Tetracarbonyl.**—A glass reaction tube 50 cm. long and 2 cm. in diameter equipped with a stopcock was flushed thoroughly with dry nitrogen. Iron pentacarbonyl (4 g., 0.02 mole) was pipetted into this tube. The reaction tube and its contents were cooled to −190°, evacuated, and flushed with nitrogen, this procedure being repeated twice. *p*-Tolylisonitrile

---

(1) L. W. Hieber and A. Thalhofer, *Angew. Chem.*, **68**, 679 (1956).
(2) W. Hieber and D. von Pigenot, *Chem. Ber.*, **89**, 610 (1956).
(3) G. Booth and J. Chatt, *J. Chem. Soc.*, 2099 (1962).
(4) T. A. Manuel, *Inorg. Chem.*, **2**, 854 (1963).
(5) W. D. Horrocks, Jr., and R. C. Taylor, *ibid.*, **2**, 723 (1963).
(6) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).
(7) F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).
(8) F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961).
(9) M. Bigorgne, *Bull. Soc. Chim. France*, 295 (1963).
(10) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).
(11) W. Hieber and G. Bader, *Chem. Ber.*, **61**, 1717 (1928).
(12) I. Ugi and R. Meyr, *ibid.*, **93**, 239 (1960).
(13) W. Hieber and D. von Pigenot, *ibid.*, **89**, 193 (1956).