TABLE VI

VALENCE FORCE CONSTANTS (MDYNES/Å.) OF $Au(CN)_4^-$

F_{CN}	17.51
F_{AuC}	2.782
$F_{CN,C'N'}$ (ad.)[a]	0.026
$F_{CN,C''N''}$ (op.)[a]	−0.060
$F_{AuC,AuC'}$ (ad.)[a]	0.035
$F_{AuC,AuC''}$ (op.)[a]	0.567

[a] The abbreviation ad. stands for adjacent (at 90°) while op. is for opposite (at 180°).

The changes are very similar to the changes for $Au(CN)_2X_2^-$; thus, the comparisons among the different Au(III) complexes in ref. 4 are still valid.

The E_u symmetry force constant for MCN bending is 0.51 mdyne Å. radian^{-2} for the new frequency assignment. With the data of ref. 8 this gives a value of 0.43 mdyne/Å. or more for the MCN valence bending constant. Thus it is still a valid point that the MCN in-plane bending constant is greater for $Au(CN)_4^-$ than for $Au(CN)_2X_2^-$ as discussed in ref. 4.

It would be possible to verify this new assignment for $Au(CN)_4^-$ by observation of the spectra of the isotopically enriched species. However, this would require higher enrichment than we have presently available. If we prepared $KAu(CN)_4$ with 60 atom % ^{13}C we would have a variety of species leading to a rather complex spectrum. Thus if all forms have equal energy, we would expect 13% $Au(^{13}CN)_4^-$, 35% $Au(^{13}CN)_3(CN)^-$, 17% cis-$Au(^{13}CN)_2(CN)_2^-$, 17% trans-$Au(^{13}CN)_2(CN)_2^-$, 15% $Au(^{13}CN)(CN)_3^-$, and 3% $Au(CN)_4^-$. It would be exceedingly difficult to as-

sign the observed peaks to the various species. Greater than 90 atom % ^{13}C would be highly desirable for such a study.

Off-diagonal Interaction Constants.—Off-diagonal interaction constants such as $F_{MC,CN}$ have been neglected. In a recent study[5] it was shown that for $Au(CN)_2^-$ $F_{MC,CN}$ is about +0.3 mdyne/Å. while $F_{MC,C'N'}$ is about zero. However, it has not yet been shown whether these interaction constants are transferable from one metal–cyanide complex to another. Further studies of isotopic species are necessary to decide this. If the MC, CN interaction constant is positive, as found for $Au(CN)_2^-$, the calculations give a higher CN force constant and a lower AuC force constant.

Summary

By a study of the ^{13}C and ^{15}N enriched species of $Au(CN)_2Cl_2^-$ and $Au(CN)_2Br_2^-$ it has been shown that the assignment of infrared-active MC stretching and MCN bending frequencies can be made unambiguously. The observations presented here show that the previous assignment[4] must be changed. New sets of force constants are given for $Au(CN)_2Cl_2^-$, $Au(CN)_2Br_2^-$, $Au(CN)_2I_2^-$, and $Au(CN)_4^-$. Other ambiguous assignments, such as the MC stretching and MCN bending frequencies of the metal hexacyanides, can be nailed down by similar studies of the isotopically enriched species. However, for species having four or more cyanides per molecule, the enrichment should be above 90 atom % to yield an interpretable spectrum.

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The Charge-Transfer Complex between Triphenylarsine and Iodine

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The 1:1 complex between triphenylarsine and iodine in carbon tetrachloride and dichloromethane solutions has been studied by spectroscopic methods in the ultraviolet, visible, and infrared regions. Formation constants, the thermodynamic functions $-\Delta F°_{298}$, $-\Delta H°$, and $-\Delta S°$, and spectral data have been obtained. Much higher formation constants were observed in the solvent dichloromethane than in carbon tetrachloride. In acetonitrile only I_3^- ions were formed, indicating a complete ionization of the complex. The ultraviolet band at 248 mμ in triphenylarsine, which has been assigned to a transition involving the lone-pair electrons, is not perturbed on complex formation to iodine.

Introduction

The compounds formed between the halogens and alkyl or aryl derivatives of group Va elements have been discussed on the basis of X-ray crystallographic determinations and from dipole and conductometric measurements in solution. X-Ray analysis of the molecules $(CH_3)_3SbX_2$ (X = Cl and Br) showed a bipyramidal configuration with X–Sb–X-type bonding.[1] The zero dipole moments of certain dichlorides support

this structure.[2] However, conductometric measurements indicate the existence of ionic species in polar solvents, and the following ionic structures have been proposed: $R_3Y^+X^-$ and $R_3Y^+X_3^-$ (Y = P, As, Sb, and Bi; X = Br and I).[3−5]

The donor properties of the alkyl or aryl derivatives

(1) A. F. Wells, *Z. Krist.*, **99**, 367 (1938).

(2) K. A. Jensen, *Z. anorg. Chem.*, **250**, 257 (1943).
(3) K. Issleib and W. Seidel, *ibid.*, **288**, 201 (1957).
(4) G. S. Harris, *Proc. Chem. Soc.*, 65 (1961).
(5) B. J. Pullman and B. O. West, *J. Inorg. Nucl. Chem.*, **19**, 262 (1961).

of group Va elements are well established through their ability to form complexes with metal salts and electron-deficient substances like BH_3 and BF_3.[6] However, no spectrophotometric measurements in solution have been reported for their complexes with the halogens.

Considerably more work has been done on the compounds formed between the sulfides, selenides, and tellurides and the halogens. Thus, spectrophotometric investigations in solution indicate that the compounds R_2SI_2[7,8] and R_2SeI_2[9,10] are of the charge-transfer type. In the solid complexes the atomic arrangements S–I–I[11] and Se–I–I[12,13] have been confirmed. In several compounds of the type $R_2(Se,Te)Br_2$, however, the bondings Br–Se–Br and Br–Te–Br have been found.[10] It should be noted, however, that in the di-*p*-chlorodiphenyltellurium diiodide[14] there are I–Te–I bonds with a tendency toward molecular complex bonding. Tetrahydroselenophene·I_2,[13] on the other hand, is a molecular complex having a tendency toward I–Se–I bonding.

In view of this, we have started a spectrophotometric investigation of the interaction between the triaryl derivatives of P, As, Sb, and Bi and the halogens. Particularly, we wanted to establish if these compounds are of the charge-transfer type and to study the relative donor strengths toward iodine. Moreover, we wanted to examine a possible ionization of the charge-transfer complexes in polar solvents.

In the present study we report a spectrophotometric investigation of triphenylarsine and iodine in carbon tetrachloride, dichloromethane, and acetonitrile. Heptane could not be used because of the low solubility of the complex in this solvent. The spectral behavior of the solid compound formed between triphenylarsine and iodine was investigated in solution. To establish the magnetic properties of the complex, e.p.r. measurements were made on the solid compound, on a mixture of solid triphenylarsine and iodine, and on triphenylarsine and iodine in solution.

Experimental

Chemicals.—Triphenylarsine from Fluka AG was purified by fractional crystallization from ethanol, m.p. 59.8–60.7°. Carbon tetrachloride, Uvasole, from Merck was dried according to Liddel,[15] and dichloromethane, Uvasole, was distilled in a Vigreux column over phosphorus pentoxide. Reagent grade iodine was sublimed from barium oxide, and acetonitrile was purified according to Wawzonek.[16]

Instrumental.—The ultraviolet and visible spectra were recorded with a Beckman DK-1 recording spectrophotometer equipped with a thermostated cell holder. Matched pairs of
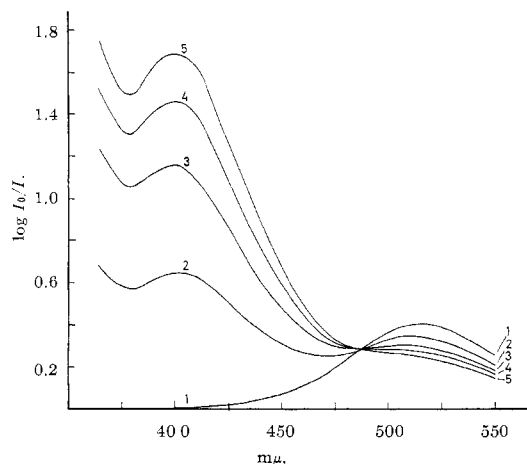
(6) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1956).

(7) H. Tsubomura and R. P. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961).

(8) M. Good, A. Major, J. Nag-Chaudhuri, and S. P. McGlynn, *ibid.*, **83**, 4329 (1961).

(9) J. D. McCullough and I. C. Zimmerman, *J. Phys. Chem.*, **64**, 1084 (1960).

(10) J. D. McCullough and D. Mulvey, *ibid.*, **64**, 264 (1960).

(11) G. Y. Chao and J. D. McCullough, *Acta Cryst.*, **14**, 940 (1961).

(12) G. Y. Chao and J. D. McCullough, *ibid.*, **13**, 727 (1960).

(13) H. Hope and J. D. McCullough, *ibid.*, **17**, 712 (1964).

(14) G. Y. Chao and J. D. McCullough, *ibid.*, **15**, 887 (1963).

(15) U. Liddel, *Ann. N. Y. Acad. Sci.*, **69**, 71 (1957).

(16) S. Wawzonek and M. E. Runner, *J. Electrochem. Soc.*, **99**, 4157 (1952).

Figure 1.—The visible absorption spectra of triphenylarsine and iodine (4.52×10^{-4} M) in carbon tetrachloride at 20° for a 1-cm. cell. The concentrations (M) of triphenylarsine are: (1) 0, (2) 2.89×10^{-4}, (3) 5.78×10^{-4}, (4) 8.67×10^{-4}, (5) 11.56×10^{-4}.

stoppered silica cells of 1-cm. path lengths were used. The infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer, having NaCl and CsBr optics. E.p.r. measurements were performed with a Varian spectrometer (Model V4500) operating at 9.5 kMc./sec. The magnetic field was modulated at 100 kc./sec.

Procedure.—A stock solution of triphenylarsine was prepared by weighing into a 100-ml. volumetric flask and by subsequent dilution of 10 ml. of this solution to 100 ml. The concentration of the iodine stock solution in carbon tetrachloride was determined from the peak absorption intensity of the visible iodine band at 517 mμ, assuming ϵ 909 l. mole^{-1} cm.$^{-1}$. Mixed solutions were made by pipetting into 25-ml. volumetric flasks.

Results

Triphenylarsine and Iodine in Carbon Tetrachloride

Solutions.—When triphenylarsine was added to a solution of iodine in carbon tetrachloride, the visible absorption band of iodine was displaced to 400 mμ. Solutions with the same iodine concentration and varying triphenylarsine concentration gave curves passing through an isosbestic point at 486 mμ, as is apparent from Figure 1. At shorter wave lengths there is also an increasing absorption with a maximum at 321 mμ, assigned as the charge-transfer band of the complex. The existence of the isosbestic point indicates that only one complex is formed. Besides, the Liptay absorption matrix,[17] normalized at the charge-transfer absorption maximum, showed no systematic variation in the ζ_{ik} values. The method of continuous variation[18] was employed to establish the stoichiometry of the complex. When the sum of the triphenylarsine and iodine concentrations was kept constant at 3.05×10^{-4} M, the Job curves showed a distinct maximum for equal concentrations of donor and acceptor, characteristic of a 1:1 complex.

The charge-transfer band was very strong and therefore well-suited for calculating the formation constant. Besides, small or no corrections for donor and acceptor absorbance were necessary. Since the complex was

(17) W. Liptay, *Z. Elektrochem.*, **65**, 375 (1961).

(18) P. Job, *Ann. Chim.*, [10] **9**, 113 (1928).

very stable, a sufficient amount of iodine was complexed without the donor concentration being much higher than the iodine concentration. Therefore, the Benesi–Hildebrand or Scott representations were not satisfied, and we calculated instead the formation constants by an iteration method. A preliminary value for K was obtained from a simplified Benesi–Hildebrand plot, this value being used to calculate the unknown concentration of the complex. The modified[9] Scott equation was then used to get a better value for K and ϵ. This procedure was repeated until a consistent set of values was obtained from two successive plots. In this particular case, only two plots were sufficient. We based our calculations on the absorbances at the charge-transfer maximum. When the spectra were recorded immediately, the measurements were reproducible to within 0.005 absorbance unit. Two or three parallel series were recorded for each temperature.

The formation constants and molecular extinction coefficients obtained at different temperatures are listed in Table I, together with one set of absorbance data

TABLE I

ABSORBANCE DATA FOR SOLUTIONS OF TRIPHENYLARSINE (D) AND IODINE IN CARBON TETRACHLORIDE AT 321 Mμ[a,b] AND THE CALCULATED FORMATION CONSTANTS, MOLAR EXTINCTION COEFFICIENTS, AND THERMODYNAMIC FUNCTIONS FOR THE COMPLEX

—— 10.2° ——		—— 20.0° ——		—— 30.0° ——		—— 40.0° ——	
3.732 × 10⁻⁵ M I₂		3.687 × 10⁻⁵ M I₂		4.916 × 10⁻⁵ M I₂		4.678 × 10⁻⁵ M I₂	
[D] × 10⁴, M	A	[D] × 10⁴, M	A	[D] × 10⁴, M	A	[D] × 10⁴, M	A
1.532	0.438	1.514	0.278	2.991	0.386	2.954	0.242
2.583	0.628	3.028	0.468	4.487	0.520	4.431	0.343
3.046	0.707	3.785	0.550	5.982	0.645	5.908	0.430
3.574	0.768	4.542	0.612	7.478	0.732	7.384	0.516
4.595	0.870	5.299	0.680	8.973	0.826	8.881	0.585
5.106	0.918	6.056	0.729	10.469	0.910	10.338	0.648
6.127	0.998	7.570	0.816	11.964	0.977	11.814	0.713
7.148	1.060	9.083	0.888	13.460	1.041	13.281	0.760
8.170	1.120	11.354	0.980	14.955	1.107	14.768	0.805
9.191	1.158	20.720	1.175	17.946	1.177	17.721	0.885

———————— K, l./mole ————————

2,420	1,400	790	490

———————— ϵ, l./mole cm. ————————

45,200	43,900	42,000	40,900

$-\Delta H° = 9.4 \pm 0.6$ kcal./mole
$-G°_{278} = 4.14 \pm 0.02$ kcal./mole
$-\Delta S° = 17.7 \pm 1.8$ e.u.

[a] For 1-cm. cell. [b] Corrections for donor and acceptor absorbance are negligible.

for each temperature. The thermodynamic functions were calculated by standard procedure. The uncertainty in $-\Delta H°$ was determined to be about 0.6 kcal./mole from an estimate of the uncertainties in the formation constants.

The complex was so stable that it should be possible to determine the extinction coefficient by using a large excess of donor. With triphenylarsine concentrations higher than 5×10^{-3} M, however, the data were not quite reproducible. With $[(C_6H_5)_3As] = 10^{-1}$ M (corresponding to 98–99% of the iodine being complexed), we found an extinction coefficient at 20° equal to 43,000 l. mole⁻¹ cm.⁻¹ at the charge-transfer

maximum, in good agreement with the results obtained by the graphical extrapolation method.

The half-intensity width $\Delta\nu_{1/2}$ of the charge-transfer band could be determined on both sides of the absorption maximum. The band was not symmetrical, but was broader on the long wave length side, in disagreement with what is generally found.[19] The half-intensity width at the long wave length side was 2050 cm.⁻¹, and at the short wave length side 1890 cm.⁻¹. Using the approximate formula for the oscillator strength,[19] we found $f = 1.2$.

Two series of triphenylarsine–iodine solutions in carbon tetrachloride were studied in the visible region, measured in a 1-cm. and a 5-cm. absorption cell, respectively. The new peak at 400 mμ is assigned as the blue-shifted iodine band. Since the extinction coefficient of the free iodine at 400 mμ is very low, K could be determined by the same method as described. The following values for K and ϵ were found at 20°: $K = 1.240$ l. mole⁻¹, ϵ (400 mμ) = 7200 l. mole⁻¹ cm.⁻¹.

This value for the formation constant is somewhat lower than obtained in the ultraviolet region. The extinction coefficient for the blue-shifted band is much larger than that of the visible iodine band for any known iodine complex. Undoubtedly there is a considerable overlap by the charge-transfer band at this wave length. The actual blue-shifted peak is therefore probably located at a somewhat longer wave length.

Dichloromethane Solutions.—Dichloromethane, being a moderately polar solvent, would possibly favor an ionization of the complex. Furthermore, this solvent is transparent to 230 mμ, making it possible to study the effect of complexation on the donor spectrum.

The spectral behavior of a solution of triphenylarsine and iodine in dichloromethane was qualitatively the same as in carbon tetrachloride. The charge-transfer band maximum was located at a somewhat shorter wave length (316 mμ). In the visible region, an isosbestic point was observed at 473 mμ, and there was an absorption maximum at 368 mμ. This band cannot be caused by a possible I_3^- absorption, since the stronger I_3^- band at 295 mμ was absent. The absorption at 368 mμ was therefore assigned as the blue-shifted band overlapped with the charge-transfer band.

An attempt to determine the formation constant by the same procedure as employed for triphenylarsine and iodine in carbon tetrachloride was not successful. Curved plots were obtained because of too small absorbance for the higher donor concentrations. The Liptay matrix, however, showed fairly constant ζ_{ik} values, indicating that only one complex is formed. Assuming the same extinction coefficient for the complex as in carbon tetrachloride, it was quite clear that the formation constant was much higher in dichloromethane than in carbon tetrachloride, contrary to

(19) G. Briegleb, "Elektronen-Donator-Acceptor-Komplex," Springer Verlag, Berlin, 1961, p. 61.

expectation. However, when the triphenylarsine concentration was kept constant at 5.7×10^{-5} M and the iodine concentration varied between 1.3×10^{-5} and 2.7×10^{-4} M, straight lines were obtained when using the Scott iteration procedure. Measurements were made at 12, 20, and 29°, and the results are listed in Table II.

TABLE II

ABSORBANCE DATA FOR SOLUTIONS OF TRIPHENYLARSINE (D) AND IODINE IN DICHLOROMETHANE AT 316 $M\mu$ AND THE CALCULATED FORMATION CONSTANTS, MOLAR EXTINCTION COEFFICIENTS, AND THERMODYNAMIC FUNCTIONS FOR THE COMPLEX

$[I_2]$ $\times$ 10^5, M^a	12.0°	20.0°	29.0°
		Absorbance[b,c]	
1.365	0.346	0.279	0.211
2.730	0.646	0.532	0.398
4.095	0.904	0.738	0.560
5.460	1.118	0.909	0.698
6.825	1.288	1.062	0.826
8.190	1.430	1.185	0.940
9.555	1.531	1.285	
10.920		1.380	1.121
12.285		1.456	
13.650			1.255
27.100			1.621

$[D]$ $\times$ 10^3, M		K, l./mole	
5,687	34,600	21,600	13,000

	ϵ, 1/mole cm.	
40,700	39,600	38,500

$$-\Delta H° = 9.9 \pm 2.0 \text{ kcal./mole}$$
$$-\Delta F°_{298} = 5.73 \pm 0.06 \text{ kcal./mole}$$
$$-\Delta S° = 14.0 \pm 7.0 \text{ e.u.}$$

a Concentrations at 20°. *b* 1-cm. cell. *c* Absorbance values are corrected for absorption of free iodine.

The ultraviolet spectrum of triphenylarsine has been studied in the region 220–340 $m\mu$.[20] In this region the spectrum consists of two band systems. In the first system three weak bands at about 270 $m\mu$ appear as inflections. They are attributed[20] to the benzene $\pi–\pi^x$ transition. The other system is structureless and appears as a strong band at 248 $m\mu$ in dichloromethane. This band (ϵ_{max} 13,100) is assigned as an intramolecular charge-transfer transition involving the arsenic lone-pair electrons and one benzene ring.[20] The solutions used for the determination of the formation constant in dichloromethane were well-suited for studying the perturbation of the 248 $m\mu$ band. There is small overlap with the charge-transfer band, and the iodine–solvent contact charge-transfer absorption was not significant at 248 $m\mu$. As is apparent from Figure 2, there was no decrease in the intensity of the 248 $m\mu$ band as the iodine concentration increased. No isosbestic points corresponding to Kubota's observations[21] were found. Below 240 $m\mu$ the mixed solutions have higher absorbance than the sum of the absorbances of uncomplexed triphenylarsine and iodine.

(20) W. R. Cullen and R. M. Hochstrasser, *J. Mol. Spectry.*, **5**, 118 (1960), and references cited therein.
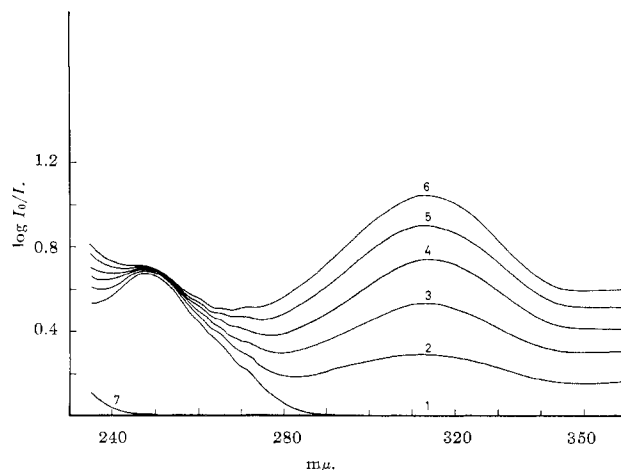(21) T. Kubota, *J. Am. Chem. Soc.*, **87**, 458 (1965).

Figure 2.—The ultraviolet absorption spectra of iodine and triphenylarsine (5.14×10^{-5} M) in dichloromethane at 20° for a 1-cm. cell. The concentrations (M) of iodine are: (1) 0, (2) 1.50×10^{-5}, (3) 3.00×10^{-5}, (4) 4.50×10^{-5}, (5) 6.00×10^{-5}, (6) 7.50×10^{-5}. Curve 7 represents the absorption of 7.50×10^{-5} M iodine in dichloromethane.

Spectral Changes with Time.—The Liptay matrix[17] constructed from absorption data in carbon tetrachloride and dichloromethane indicated that, at least in solutions with low $[(C_6H_5)_3As]/[I_2]$ ratios, small amounts of the I_3^- ions were formed, because the ζ_{ik} values around 295 and 365 $m\mu$ for these solutions were higher relative to those with a larger $[(C_6H_5)_3As]/[I_2]$ ratio. A few hours later this tendency was much more pronounced and an increase in the absorbance at 295 and 365 $m\mu$ was observed, accompanied by a decrease in the absorption of the charge-transfer band. After 8 hr. in darkness the charge-transfer absorption decreased by approximately 5%. If the mixed solutions were exposed to daylight, these reactions went much faster. After 3 hr. most of the complex was destroyed, resulting in the two distinct I_3^- bands. From the reported extinction coefficient for these bands,[22] it appears that approximately two molecules of iodine gave one I_3^- ion. These spectral changes were accompanied by a decrease in the absorbance of the donor band at 248 $m\mu$. A slow ionization of the complex followed by dissociation might be the reason for the formation of the triiodide ion. This explanation is contradicted by the fact that the reaction is almost as rapid in the nonpolar solvent carbon tetrachloride as in the polar solvent dichloromethane.

Acetonitrile Solutions.—In a solution of triphenylarsine and iodine in acetonitrile no charge-transfer complex was detected. Instead, bands at about 290 and 360 $m\mu$ indicated the presence of I_3^- ions. This may suggest that the charge-transfer complex, initially formed, very quickly undergoes an ionization, followed by the formation of I_3^- from reaction between I^- and iodine. The net result would be $(C_6H_5)_3As \cdot I_2 + I_2 \rightleftharpoons (C_6H_5)_3I^+I_3^-$. This mechanism would imply that one triphenylarsine molecule gives one I_3^- ion, and the concentration of this species should not exceed the

(22) R. E. Buckles, J. P. Yuk, and A. I. Popov, *ibid.*, **74**, 4379 (1952).

initial concentration of triphenylarsine. However, with excess of iodine, I_3^- ions in more than equivalent amounts are formed, indicating that some other reaction also takes place.

The assumption that $(C_6H_5)_3AsI^+I_3^-$ is formed in polar solvents is consistent with conductometric studies.[4,5] We think, however, in light of what was observed spectrophotometrically, that quantitative considerations based upon conductometric measurements might be difficult.

The Solid Triphenylarsine–Iodine Compound in Solution.—The solid compounds triphenylarsine diiodide and triphenylarsine tetraiodide have been reported.[23] Following the procedure by these authors, we obtained only one compound, orange-brown, m.p. 130–140°. This substance was obviously the same as the tetrahalide reported by Jensen, et al.[24] The structure $(C_6H_5)_3AsI^+I_3^-$ has been suggested for this adduct.[25] We found, however, that when dissolving the substance in carbon tetrachloride or dichloromethane the intense bands with maxima at 321 and 316 mμ, respectively, were observed.

The spectra of different concentrations of the solid compound were recorded in the two solvents. The dissociation constants were calculated, assuming the same extinction coefficients as listed in Tables I and II, and tentatively assuming 1:1 stoichiometry for the solid compound. Qualitatively good agreement was obtained in both solvents with the formation constants for the charge-transfer complex in solution. Although no firm conclusion about the stoichiometry of the solid compound can be drawn on this basis, it is obvious that the substance behaves as a compound of the charge-transfer type, dissociating in nonpolar and moderately polar solvents into its components. The spectra indicate that it is very unlikely that the substance is an arsine iodide–triiodide.

The Infrared Region.—When iodine was added to a solution of triphenylarsine in carbon disulfide, the band at 474 cm.$^{-1}$ became broader. At high iodine concentration this band appeared as a shoulder on a new peak at 466 cm.$^{-1}$. This supports the assumption that the complex formation takes place from the As atom, since the 474 cm.$^{-1}$ band is assigned to an asymmetrical $C_3\!\!\equiv\!\!As$ stretching mode.[24] No further spectral shifts were observed in the region 1400–400 cm.$^{-1}$, but the weak bands at 1333, 1304, 1271, and 1184 cm.$^{-1}$ were enhanced.

Electron Paramagnetic Resonance.—Some qualitative e.p.r. measurements were performed. The solid triphenylarsine–iodine compound gave no detectable e.p.r. signal. Neither were any effects observed for triphenylarsine and iodine in carbon tetrachloride or dichloromethane. However, in concentrated acetonitrile solutions a weak e.p.r. signal was detected.

Discussion

The observations made in the ultraviolet, visible, and infrared regions can be explained in terms of a (n,σ) charge-transfer complex between triphenylarsine and iodine. Both the equilibrium constant and the heat of formation, together with the large blue shift of the visible iodine band, indicate a very strong interaction, excluding the possibility of a π complex from the benzene rings. The corresponding diphenyl selenide complex with iodine has been studied spectrophotometrically,[26] and diphenyl selenide seems to be a much weaker donor toward iodine than triphenylarsine. This large difference is probably caused by the lack of conjugation in triphenylarsine, thus making the lone-pair electrons more available for donation than in the selenide. In fact triphenylarsine is one of the strongest donors toward iodine known, surpassed only by the tertiary amines,[27] while alkyl selenides,[7–10] thiourea and thioacetamide,[28] and tribenzylamine N-oxide and trimethylamine N-oxide[21] give comparable heats of formation. The extinction coefficient for the charge-transfer band is one of the highest ever measured and of comparable magnitude with those found in thiourea and thioacetamide with iodine.[28]

Generally, the formation constant for a nonionic charge-transfer complex decreases when going from a nonpolar solvent to a solvent with a higher dielectric constant.[29] In the triphenylarsine–iodine system, however, the formation constant is much higher in dichloromethane than in carbon tetrachloride, an effect we have not seen reported earlier. The higher frequency of the absorption maximum for the charge-transfer band in the former solvent is also contrary to expectations,[30] as charge-transfer bands usually are red-shifted in solvents with higher dielectric constants. This is generally attributed to solvent interaction, which should reduce the energy of the highly polar (excited) state. If, however, the contribution of the dative structure to the ground state in the present complex is very high (more than 50%), a polar solvent would reduce the energy of the ground state relative to that of the excited state, and the blue shift when going from carbon tetrachloride to dichloromethane might be explained.

The higher solvation energy for the complex in dichloromethane as compared to carbon tetrachloride might moreover account for the large formation constant in the former solvent. The measured heat of formation really seems to be higher in dichloromethane, as is apparent from Tables I and II. This is also indicated by the relative magnitude of the blue shift of the iodine band. However, if the stability of the complex in dichloromethane is due to the more negative $\Delta H°$, we should expect a more negative $\Delta S°$ in this solvent. Unfortunately, the determination of the heat of

(23) W. Steinkopf and G. Schwen, *Ber.*, **54**, 1461 (1921).
(24) K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, **17**, 1875 (1963).
(25) E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 215.

(26) J. D. McCullough, *J. Am. Chem. Soc.*, **64**, 2672 (1942).
(27) H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, **33**, 1660 (1960).
(28) R. P. Lang, *J. Am. Chem. Soc.*, **84**, 1185 (1962).
(29) Reference 19, p. 118.
(30) Reference 19, p. 37.

formation in dichloromethane is not very accurate. If we assumed a value of $-\Delta H° = 11.5$ kcal./mole, which is within the experimental uncertainty, it would account for the high formation constant and give relative magnitudes for the entropies of formation which are reasonable.

When an electron pair is involved in charge-transfer bonding, one should expect a lowering of the nonbonding orbital energy, giving rise to a blue shift for the n–π^x transition, in analogy with observations in hydrogen-bonded systems. Experimental conditions, however, usually make it difficult to observe the influence of the acceptor on the donor absorption bands. In the complex between pyridine N-oxide and iodine in dichloromethane, Kubota[21] observed that the donor band at 284 mμ was shifted to 275 mμ in the complex. Strong evidence is given for assigning the 248 mμ band in triphenylarsine as a transition involving the arsenic lone-pair electrons. The apparent lack of perturbation of this band, therefore, is surprising.

It is found that a paramagnetic complex is formed when triphenylamine interacts with iodine, both in the solid and the liquid states.[31] The donor positive radical ion was identified. As triphenylamine undoubtedly is a very weak base toward iodine,[5] these observations seem surprising. Because triphenylarsine is a much stronger donor toward iodine, one might expect a definite paramagnetic behavior in this system. Although no quantitative data were obtained from the weak signal in concentrated acetonitrile solution, it is obvious that the present system shows a negligible e.p.r. resonance compared to the triphenylamine-iodine compound. The connection between e.p.r. behavior and the strength of charge-transfer complexes is not clear. More work undoubtedly has to be done before the mechanisms involved can be elucidated.

(31) D. N. Stamires and J. Turkevich, *J. Am. Chem. Soc.*, **85**, 2557 (1963).

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The Nature of Vanadate(V) Solute Species in Alkaline Solution

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Light-scattering measurements have been made on two series of sodium vanadate solutions, the total vanadium concentration being varied from 0.01 to 0.20 M. The first series was made up with a sodium to vanadium molar ratio of 1:1, corresponding to what is referred to commonly as sodium metavanadate, and is found to be tetrameric, in agreement with most previous findings. The second series contained a sodium to vanadium molar ratio of 2:1, corresponding to sodium pyrovanadate, and is found to be dimeric.

Introduction

The nature of solute vanadate species in aqueous solutions above pH 7 has been reviewed adequately as of 1964 by Ingri and co-workers.[1,2] For salts which we shall call sodium vanadate (2:1), commonly known as sodium pyrovanadate, there is general agreement that the vanadate species is a dimer in all but very dilute solutions.

For solutions of sodium vanadate (1:1), commonly known as sodium metavanadate, there is somewhat less agreement. The most recent work of Ingri and co-workers[2] proposes that both tetrameric and trimeric solute species are present, the former predominating at ordinary concentrations, and the latter becoming important in the 10^{-3} M total vanadium range. Very recently Naumann and Hallada[3] confirmed earlier work that the metavanadate behaves as though it is tetrameric in molten Glauber's salt.

We wish to report the results of light scattering measurements on the two series of vanadate solutions.

Experimental

Stock Solutions.—G. F. Smith Chemical Co. sodium perchlorate was recrystallized twice from water, dissolved, and brought to a pH of 2 with dilute HClO$_4$. The resulting solution was evaporated to the desired concentration under an atmosphere of N$_2$ gas. The final pH was adjusted to 6 with microdrops of concentrated aqueous NaOH. Stock solutions prepared in the foregoing manner were stored in polyethylene bottles and showed no turbidity when treated with BaCl$_2$ or AgNO$_3$.

Stock solutions of NaOH were prepared by dissolving J. T. Baker Chemical Co. pellets in carbonate-free distilled water. Stock HClO$_4$ solutions were made by simple dilution of J. T. Baker 70–72% HClO$_4$.

Fisher Scientific Co. sodium metavanadate was found to have other than a 1:1 molar ratio of Na to V. Even so, stock solutions were prepared of "metavanadate" by dissolving the commercial sample in enough water to give *ca.* 0.5 M vanadium. Sodium vanadate (1:1) stock solution was prepared by adding calculated amounts of molar NaOH to Fisher Scientific Co. vanadium pentoxide. The solution was stirred for 48 hr. at 60°.

Analyses.—Stock NaOH solutions were standardized with

(1) N. Ingri and F. Brito, *Acta Chem. Scand.*, **13**, 1971 (1959).
(2) F. Brito, N. Ingri, and L. G. Sillén, *ibid.*, **18**, 1557 (1964).
(3) A. W. Naumann and C. J. Hallada, *Inorg. Chem.*, **3**, 70 (1964).