Electronic Structures of Arsines and Phosphines

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Abstract: Electronic spectra of *o*-phenylenebisdimethylarsine (diars) have been studied at 300 and 77°K. Electronic spectra of the molecular complexes of various substituted organoarsines and triphenylphosphine with tetracyanoethylene have been measured and used to estimate the relative ionization potentials of these molecules. Uv photolysis of arsines in frozen solution (96°K) has yielded thermally labile, paramagnetic products. These products include the molecular cations of the photolyzed compounds as well as radical species of the type ($R_2\ddot{A}s\cdot$). The electron spin resonance spectrum of (diars)$^+$ exhibits hyperfine splitting due to two equivalent ^{75}As ($I = {}^3/_2$) nuclei. The data indicate that the unpaired electron in (diars)$^+$ is thoroughly delocalized over its π orbital network.

We have been concerned lately with the elucidation of the electronic structures of transition metal complexes containing the bidentate, arsenic-donor ligand *o*-phenylenebisdimethylarsine (diarsine or diars).[3,4] Parallel to this effort, we have studied the electronic structure of diarsine itself, as well as several other arsines and phosphines.

In this paper we report the electronic spectra of diarsine and charge-transfer complexes of substituted arsines and triphenylphosphine with tetracyanoethylene. We also present electron spin resonance spectra and discuss the electronic structures of radicals produced by uv photolysis of the arsines at 96°K.

Experimental Section

Compounds. *o*-Phenylenebisdimethylarsine (diarsine) was prepared and purified by the method of Feltham[5] [bp 102–106° (1 mm)] or obtained from City Chemical Co. or Aldrich Chemical Co. and used without further purification. The purity of the sample was checked by nmr and uv spectroscopy. The sample obtained from City Chemical Co. was found to be decomposed after standing for several months. If refrigerated and protected from oxygen, diarsine will not significantly decompose for many months. Triphenylarsine and triphenylphosphine were both reagent grade chemicals, obtained from Aldrich and Matheson Coleman and Bell. Tetracyanoethylene was an Eastman Organic Chemicals White Label reagent.

Dimethyliodoarsine was prepared by the method of Burrows and Turner[6] and used without further purification. Bis(diphenylarsino)ethane was obtained from Strem Chemicals.

Spectral Measurements. The ultraviolet absorption spectral measurements were made on a Cary 14 RI spectrophotometer, using 1.00-cm square cells of fused Suprasil. Measurement of spectra at 77°K was carried out with a quartz dewar which allowed complete immersion of the sample. Bubbling of the liquid nitrogen under operating conditions was prevented by cooling to 75°K under reduced pressure.

Freshly prepared EPA (5 parts ethyl ether–5 parts isopentane–2 parts ethanol) was used as solvent for the low-temperature measurements. The ethanol was anhydrous USP-NF grade (U. S. Industrial Chemical Co.), the ethyl ether was anhydrous reagent grade (Mallinckrodt), and the 2-methylbutane was spectroquality (Matheson Coleman and Bell). Chloroform used in the spectral studies of the charge-transfer complexes was spectroquality (MCB).

Preparation of Samples for Uv Photolysis–Esr Experiments. Solutions were mixed under nitrogen atmosphere and in air. The experimental results indicated no need for preparing the samples under nitrogen. All solutions were thoroughly outgassed on an oil diffusion-pumped vacuum system prior to being sealed in cylindrical quartz esr tubes (3 mm i.d.). To ensure that no detectable esr signals originated from the quartz tubes or the quartz dewar used as a sample tube holder in the cavity, blank tests were carried out on them in the presence and absence of uv irradiation.

Uv Photolysis of Samples. All samples were irradiated with a high pressure mercury–xenon source (Hanovia, 2.5 kW, compact arc) filtered through a 0.1 *M* aqueous cobalt(II) chloride solution to remove visible and infrared radiation. The light used in the irradiations consists of a broad band in the region 210–450 nm, with maximum intensity in the range 300–400 nm. The filtered light beam was collimated by a series of quartz lenses and focused on the sample, which was located in the center of the front compartment of the esr cavity. A hole in the front of the cavity covered with a quartz faceplate allowed access of the light beam. Using this apparatus, irradiation may be carried out during the course of the esr experiment, or, alternatively, the beam may be blocked while the spectrum is recorded.

Esr Measurements. Esr measurements at X-band (9.2 GHz) were carried out on a Varian V-4502 spectrometer system employing 100-kHz field modulation and a 9-in. Varian electromagnet with Fieldial. This system was equipped with a V-4532 dual sample cavity. Microwave frequencies were measured directly using a wave meter attached to one arm of the "Magic Tee" detection system. The magnetic field was calibrated by the measurement of a standard sample of diphenyldipicrylhydrazyl (K and K Chemical Co.) in benzene, which was placed in the rear compartment of the dual cavity assembly. This calibration was carried out simultaneously with every spectrum measured, by using low frequency (20–400 Hz) modulation and detection. Temperature control was achieved using the Varian V-4540 variable temperature controller. Cooling of the sample was effected by blowing a stream of pure nitrogen gas, which was first passed through a liquid nitrogen heat exchanger, through a small quartz dewar, which sits in the esr cavity and holds the sample tube. Calibration of the temperature controller was carried out using a standard copper–constantin thermocouple and a Leeds and Northrup millivolt potentiometer. The lowest temperature accessible under operating conditions was found to be 96°K.

Results

Electronic Spectral Measurements on Diarsine. The results of the spectral study are set out in Table I.

Table I. Electronic Absorption Spectra of Diarsine[a]

T = 300°K	T = 77°K
35,000–40,000 (400–4000)[b]	(WS) 35,160 (1280)
	(WS) 36,385 (2620)
	(WS) 37,398 (3630)
	(WS) 38,490 (4460)
	41,036 (9150)

[a] $\bar{\nu}$, cm^{-1} (ϵ, l. mol^{-1} cm^{-1}). EPA solvent (5:5:2 mixture of ethyl ether, isopentane, and ethanol). [b] Featureless, rising absorption.

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[3] J. R. Preer and H. B. Gray, *J. Amer. Chem. Soc.*, **92**, 7306 (1970).

[4] P. Kreisman, R. Marsh, J. R. Preer, and H. B. Gray, *ibid.*, **90**, 1067 (1968).

[5] R. D. Feltham, A. Kasenally, and R. S. Nyholm, *J. Organometal. Chem.*, 7, 285 (1967).

[6] G. J. Burrows and E. E. Turner, *J. Chem. Soc.*, 117, 1376 (1920).

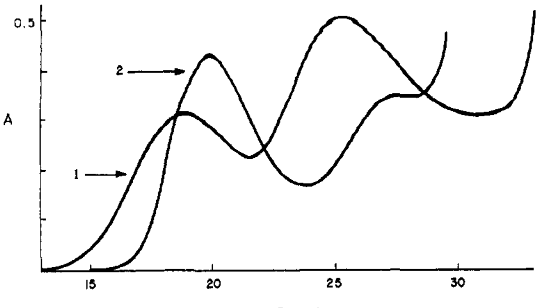

Figure 1. Electronic spectra of charge-transfer complexes in $CHCl_3$· 1-[$(C_6H_5)_3As$·TCNE] and 2-[$(C_6H_5)_3P$·TCNE].

The weak shoulders which appear on the low energy side of the main absorption in the low-temperature spectrum are assigned as the vibronic structure of the $\pi \rightarrow \pi^*$ transition localized on the benzene ring. The main absorption at 41,036 cm^{-1} is assigned as a charge-transfer transition involving excitation of an essentially nonbonding As electron to the π^* level of the benzene ring. Analogous assignments for $(C_6H_5)_3Q$ (Q = As, P) have been given previously by Cullen and Hochstrasser.[7]

Charge-Transfer Complexes. The charge-transfer complexes of triphenylarsine or triphenylphosphine with tetracyanoethylene (TCNE) appear to be quite stable in solution; they were prepared by simply dissolving the two components together in chloroform. The spectra of the charge-transfer complexes of $(C_6H_5)_3Q$ with TCNE are pictured in Figure 1. Note that two absorption bands appear where neither donor nor acceptor alone absorbs. Complete results of the visible spectral study of the charge-transfer complexes are given in Table II.

Table II. Electronic Absorption Spectra of Molecular Complexes[a]

Donor	Acceptor	λ_{max}, nm	$\bar{\nu}$, cm^{-1}
$(C_6H_5)_3N$	TCNE	866	11,545
		415	24,095
$(C_6H_5)_3P$	TCNE	502	19,915
		374	26,750
$(C_6H_5)_3As$	TCNE	530	18,885
		394	23,345
$[(C_6H_5)_2AsCH_2]_2$	TCNE	532	18,795
		402	24,875
Diarsine	TCNE	580	17,225
		428	23,390

[a] Measured in $CHCl_3$ solution, 300°K.

Varying the proportion of TCNE to donor does not seem to affect either the band positions or the absorbance ratio of the two bands exhibited by the charge-transfer complex. The charge-transfer complex of TCNE with diarsine is considerably less stable than the other two studied but can be prepared and studied in the same way. The stability of the (diarsine·TCNE) charge-transfer complex is strongly solvent dependent. In chloroform, the blue color of the freshly prepared complex persists for over 5 min. By working rapidly and carrying out the measurement in sections, a reasonably reproducible spectrum was obtained. In ethanol, the solution becomes yellow immediately, due to the formation of the stable radical anion (TCNE)$^-$. Carrying out the charge-transfer-complex-forming reaction in the absence of oxygen and light did not lead to noticeably increased stability. At liquid nitrogen temperature, the equilibrium of eq 1 is shifted far to the

$$\text{diars} + \text{TCNE} \overset{K}{\rightleftharpoons} (\text{diars}\cdot\text{TCNE}) \qquad (1)$$

right and the complex appears to be stable for many hours.

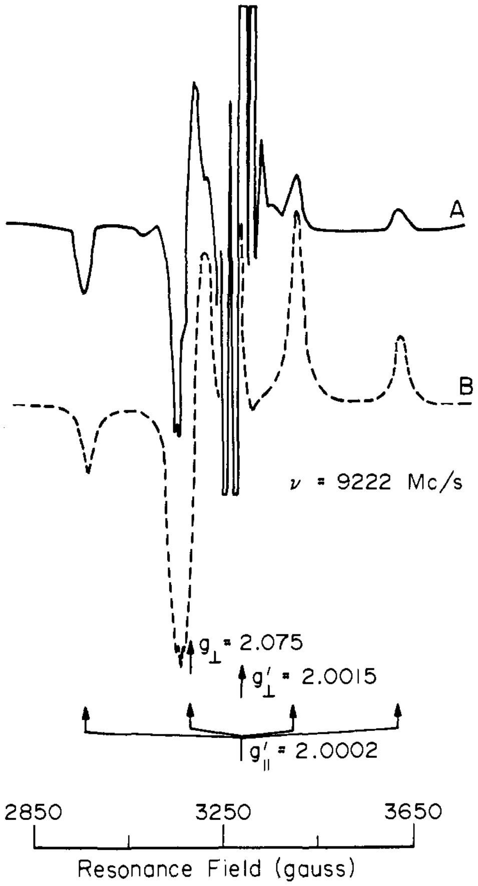

Figure 2. Observed (A) and simulated (B) esr spectra for uv-irradiated diarsine in ethanol (96°K). The signal at g = 2.075 is assigned to (diars)$^+$, and the remaining signals (indicated by arrows) are assigned to $[(CH_3)_2\dot{A}s\cdot]$.

Diarsine does not form a charge-transfer complex with p-benzoquinone in chloroform solution. An attempt was made to study the charge-transfer complex of diarsine with tetrachloro-p-benzoquinone (chloranil). At high concentrations of chloranil, a blue complex appears, and at lower concentrations, a red form is present. In a matter of a few minutes at room temperature, the diarsine–chloranil system in chloroform loses its initial color and deposits colorless crystals. After several hours, a black solid separates from the deep purple solution which is formed. Because of these complications, we have not studied this system further. However, detailed mechanistic studies have been carried out on the reactions of a similar system involving chloranil and dimethylaniline.[8]

Uv Photolysis–Esr Experiments. *o*-Phenylenebisdimethylarsine (Diarsine). The esr spectrum of a 0.1 M frozen solution of diarsine in ethanol (T = 96°K) after

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[7] W. R. Cullen and R. M. Hochstrasser, *J. Mol. Spectrosc.*, **5**, 118 (1960).

[8] E. M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 81 (1965).

uv photolysis for 2 min (210 nm $< \lambda <$ 450 nm) is shown in Figure 2 (spectrum A). Examining the signal centered at $g = 2.075$ by expanding the scale (Figure 3) reveals seven overlapping hyperfine lines with a coupling constant of 11.5 G. The esr spectrum (see Figure 2) is rather complicated and it seems unlikely that all the signals arise from a single radical species. Additional information concerning the origin of these signals may by derived from esr measurements we have carried out in various other solvents, including methylcyclohexane, 3:2 isopentane–methylcyclohexane (MP), and 6:5 ethanol–methanol.

The esr signals observed for diarsine in these solvents fall into two distinct groups; those narrow in line width and strongly dependent on solvent and those broad in line width and independent of solvent. The signals which are solvent dependent were also found to exhibit isotropic g values and hyperfine components with splittings close to those expected for protons, indicating that they must originate from the solvent. In contrast, the solvent-independent signals were found to have anisotropic g values and hyperfine components characteristic of a nuclear spin of $^3/_2$, and therefore they are logically assigned to arsenic-containing radicals originating from diarsine.

Except for the solvent-dependent region near $g = 2.00$, the esr spectrum of diarsine irradiated at 96°K exhibits line shapes characteristic of a superposition of the individual, angularly dependent resonances corresponding to different orientations of paramagnetic centers in a powder or frozen-glass sample. Such a spectrum is commonly observed for a polycrystalline sample in which the randomly oriented paramagnetic species are known to possess anisotropic g tensors and/or nuclear hyperfine tensors. As diarsine is a good electron donor, one expected photoreaction is

$$(\text{solvent}\cdot\text{diars}) \xrightarrow{h\nu} (\text{solvent})^-(\text{diars})^+$$

The seven-line signal at $g = 2.075$ may be assigned to $(\text{diars})^+$, which would have two equivalent ^{75}As nuclei ($I = {}^3/_2$; $2I + 1 = 7$). The line shapes of the signals centered at $g_{||}' = 2.0002$ indicate that they arise from the parallel hyperfine components of a radical species containing a single arsenic atom. Presumably, the fourth hyperfine line is buried under the strong signal at $g = 2.075$. We assign the $g_{||}' = 2.0002$ hyperfine components to the radical species $[(\mathrm{CH_3})_2\dot{\mathrm{A}}\mathrm{s}\cdot]$, on the ground that cleavage of one of the phenyl–arsenic bonds [D(As–C) = 51–61 kcal mol^{-1}][9] in photoexcited diarsine is a reasonable primary pathway for nonradiative decay. The bond dissociative pathway would also produce a substituted phenyl radical, $[\cdot\mathrm{C_6H_4As(CH_3)_2}]$, which would be expected to react rapidly with solvent to yield one or more radicals with signals in the $g = 2.00$ region.

A computer-simulated spectrum for the solvent independent region employing a method described elsewhere[10] is presented in Figure 2 along with the observed spectrum for comparison. The simulated spectrum assumed the presence of $(\text{diars})^+$ and $[(\mathrm{CH_3})_2\dot{\mathrm{A}}\mathrm{s}\cdot]$ in 3:20 ratio and employed a Lorentzian line shape of constant line width. Simulated spectrum C in Figure 3 shows the seven partially resolved hyperfine components centered at $g = 2.075$. The relative intensities of 1:2:3:4:3:2:1 in this spectrum are calculated for two equivalent arsenic nuclei of $(\text{diars})^+$.[11] The results of this spectral analysis are summarized in Table III.

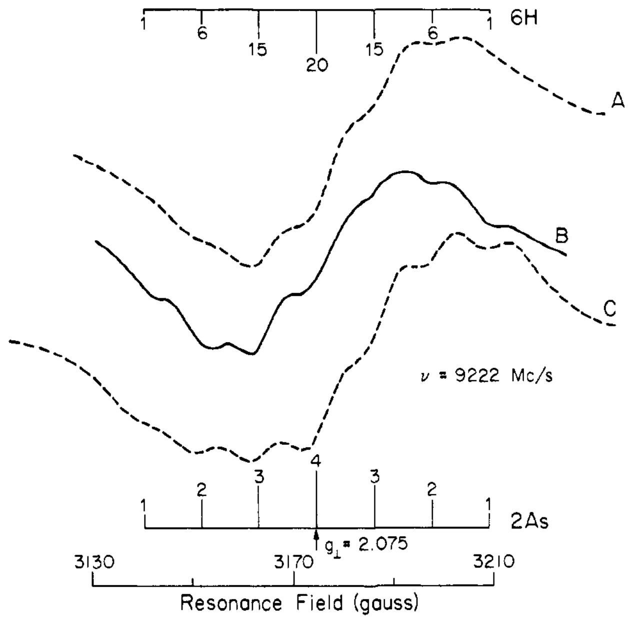

Figure 3. Observed and simulated esr spectra of $(\text{diars})^+$ (spectra B, C). A computer-simulated spectrum based on the presence of proton hyperfine structure due to six equivalent protons of $[(\mathrm{CH_3})_2\dot{\mathrm{A}}\mathrm{s}\cdot]$ is also shown (spectrum A). For comparison, the relative intensities of the seven hyperfine components arising from six equivalent protons and from two equivalent arsenic nuclei are shown.

We next turn our attention to the fate of the $(\text{solvent})^-$ radical formed as part of the $(\text{solvent})^-(\text{diars})^+$ photoproduct. Apparently, $(\text{solvent})^-$ rapidly reacts to give a neutral radical and a diamagnetic anion, because we have not been able to identify a proton hyperfine splitting pattern attributable simply to $(\text{solvent})^-$. In this regard a particularly revealing experiment is the uv irradiation of diarsine neat at 96°K. In this one-component system diarsine must function as both donor and acceptor and the portion of the esr spectrum near $g = 2.00$, in which solvent radicals generally appear, exhibits the four-line spectrum characteristic of methyl radical. Smaller and Matheson report $\langle A_\mathrm{H}\rangle = 27$ G for $(\mathrm{CH_3}\cdot)$ in solid methane (20°K) and $\langle A_\mathrm{H}\rangle = 25$ G for uv-irradiated $(\mathrm{CH_3})_2\mathrm{Hg}$ (77°K).[12] In irradiated diarsine, we measure $\langle A_\mathrm{H}\rangle = 24.1$ G (96°K). Presumably the $(\text{diars})^-$ formed undergoes dissociative electron attachment to give methyl radical plus the diamagnetic anion $[o\text{-}\mathrm{C_6H_4As(CH_3)_2}$-

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(9) F. I. Vilesov and V. M. Zaitsev, *Dokl. Akad. Nauk SSSR*, **154**, 886 (1964).

(10) F. D. Tsay, H. B. Gray, and J. Danon, *J. Chem. Phys.*, **54**, 3760 (1971).

(11) We considered the possibility that the seven hyperfine components centered at $g = 2.075$ arise from the six equivalent protons of $[(\mathrm{CH_3})_2\dot{\mathrm{A}}\mathrm{s}\cdot]$ rather than from the two arsenic atoms in $(\text{diars})^+$. The available spectral evidence rules against this interpretation, primarily because a computer simulated spectrum (A, Figure 3) based on a 11.5-G proton hyperfine constant and 6.0-G line width (taken from the observed spectrum) exhibits an effective five-line pattern. A five-line pattern results in this simulated spectrum because the intensity ratio of the seven proton hyperfine lines is 1:6:15:20:15:6:1 and the two outermost components are extremely weak. Furthermore, the intensity ratio g perpendicular–g parallel cannot be interpreted on the basis of a single species. This ratio has also been found to vary with other substituted arsines we have studied.

(12) B. Smaller and M. S. Matheson, *J. Chem. Phys.*, **28**, 1169 (1958).

Table III. Electron Spin Resonance Data for Uv-Irradiated Arsines

	Triphenylarsine		Bis(diphenylarsino)ethane		Diarsine		Dimethyliodoarsine	
	$[(C_6H_5)_3\ddot{\mathrm{As}}]^+$	$[(C_6H_5)_3\ddot{\mathrm{As}}\cdot]$	$[(C_6H_5)_2\ddot{\mathrm{As}}CH_2]_2^+$	$[(C_6H_5)_2\ddot{\mathrm{As}}\cdot]$	$[\mathrm{diars}]^+$	$[(CH_3)_2\ddot{\mathrm{As}}\cdot]$	$[(CH_3)_2AsI]^+$	$[(CH_3)_2\ddot{\mathrm{As}}\cdot]$
$g_\parallel$	2.063	2.000	2.063	2.000	2.070	2.000	2.070	2.000
$g_\perp$	2.074	2.002	2.072	2.002	2.075	2.002	2.075	2.002
$g_\perp'$	2.079		2.078					
A	3.0 G	220 G	3.0 G	220 G	9.5 G	220 G	20.0 G	220 G
B	4.0 G	5.0 G	4.0 G	5.0 G	11.5 G	5.0	22.0 G	5.0 G
Line width[a]	5.0 G	7.0 G	5.0 G	7.0 G	6.0 G	8.0 G	14.0 G	30.0 G
Ratio[b]	3:25		2:25		3:20		3:50	

[a] Line width of Lorentzian line shape used in simulating the spectrum. [b] Molecular radical cation/$(R_2\ddot{\mathrm{As}}\cdot)$.

$AsCH_3]^-$. The known stability[13] of divalent arsine anions of the type $(R_2As)^-$ is consistent with this interpretation.

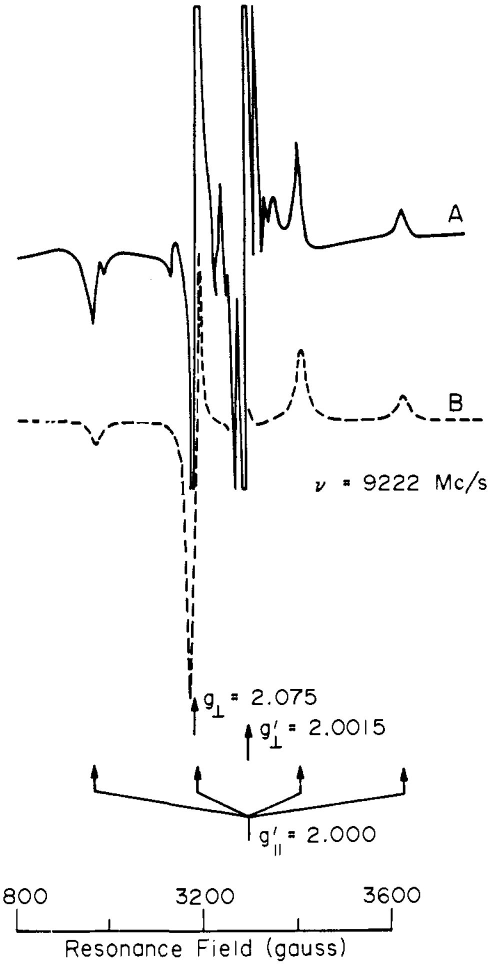

Figure 4. Observed (A) and simulated (B) esr spectra of uv-irradiated $(C_6H_5)_3As$ in ethanol (96°K). The signal at g = 2.075 is assigned to $[(C_6H_5)_3As]^+$, and the remaining signals (indicated by arrows) are assigned to $[(C_6H_5)_2\ddot{\mathrm{As}}\cdot]$.

In ethanol, the solvent radical exhibits a regular five-line pattern ($\langle A_H \rangle$ = 24.5 G), with each line showing incipient further splitting to a doublet. A quintet has been observed in the esr spectrum of γ-irradiated ethanol ($\langle A_H \rangle$ = 22.3 G) and assigned to the radical CH_3CHOH.[12] We assign the quintet observed here to the same species. In some cases, the ethanol solution seems to exhibit a triplet instead of a quintet. Closer examination reveals the outer lines of the quintet, with $\langle A_H \rangle$ = 23.5 G. Further evidence for these assignments is provided by our observation that each of the quintet lines shows incipient further splitting to a doublet $\langle A_{H'} \rangle$ = 4–6 G, which is presumably due to the hydroxyl proton.

In methylcyclohexane, the solvent radical region is extremely complicated and it appears that more than one radical is produced. In the mixed solvent MP, however, methyl radical dominates. Production of methyl radical is in all likelihood accompanied by formation from isopentane of the secondary carbanion $(CH_3\ddot{C}HCH_2CH_2)^-$.

Triphenylarsine. The esr spectrum of a uv-irradiated sample of triphenylarsine in ethanol is shown in Figure 4, together with the computer-simulated spectrum for 3:25 $[(C_6H_5)_3As]^+/[(C_6H_5)_2\ddot{\mathrm{As}}\cdot]$. The results of this spectral analysis are summarized in Table III. The gross features of the spectrum are remarkably similar to those observed for diarsine. The positions of all the corresponding maxima and minima, and of the main arsenic radical signal, are all nearly identical in the two cases. The appearance of the main signal ($g \approx 2.07$), however, is different. This signal is narrow in line width and displays a line shape with rhombic g values and perhaps some unresolved arsenic hyperfine structure. The fact that the region around g = 2.07 is rather different for irradiated diarsine and $(C_6H_5)_3As$, both in the hyperfine splitting and in the symmetry of g, is additional evidence that this signal in each case should be attributed to the respective molecular cation.

Bis(diphenylarsino)ethane. The positions and shapes of all signals in the esr spectrum of this compound irradiated at 96°K in a 1:1 ethanol–toluene glass are virtually indistinguishable from those of triphenylarsine (Figure 4). The only difference between the two cases is the ratio of peak heights of the signal at 3200 G, corresponding to the molecular cation, and that at 2970 G, corresponding to one component of the spectrum of $(R_2\ddot{\mathrm{As}}\cdot)$. The results for irradiated bis(diphenylarsino)ethane are listed in Table III.

Dimethyliodoarsine. The general features of the esr spectrum of an ethanol solution of this compound uv-irradiated at 96°K are the same as in all the other cases. A comparison of experimental and computer-simulated spectra is presented in Figure 5. The simulated spectrum (A, Figure 5), assuming the presence of only $[(CH_3)_2\ddot{\mathrm{As}}\cdot]$ with $g_\parallel$ = 2.000, $g_\perp$ = 2.075, A = 220 G, B = 5 G, and line width = 30 G, does not appear to

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(13) J. R. Phillips and J. H. Vis, *Can. J. Chem.*, **45**, 675 (1967).

match the experimental spectrum. In particular, the region near $g = 2.075$ is poorly represented; the other simulated spectrum (C, Figure 5), based on the presence of $[(CH_3)_2AsI]^+/[(CH_3)_2\ddot{A}s\cdot]$ in 3:50 ratio with the esr parameters listed in Table III, is in satisfactory agreement with that observed experimentally. The increased relative production of $[(CH_3)_2\ddot{A}s\cdot]$ in irradiated $(CH_3)_2AsI$ is in accord with the low energy of the As–I bond (49 kcal mol^{-1}).[14]

Triphenylphosphine. Uv irradiation of a solution of triphenylphosphine in ethanol at 96°K results in the slow appearance of the typical ethanol radical esr signal of five sharp lines. No other signal can be detected. Prolonged irradiation of ethanol alone gives a weak, asymmetric, one-line esr signal. It is probable that electron transfer from triphenylphosphine to the solvent leads to the five-line spectrum. We expect to see a doublet from $[(C_6H_5)_3P]^+$, but this feature is not observed. Most likely $[(C_6H_5)_3P]^+$ is formed initially but reacts too rapidly to be observed under these experimental conditions.

Discussion

Electronic Spectral Studies. Electronic absorption spectroscopy is the principal physical method for obtaining information about the electronic structures of charge-transfer complexes.[8,15–19] McConnell and coworkers have pointed out the relationship between the energy of the charge-transfer transition in the spectrum of the complex and the ionization potential of the donor molecule.[15] They found that if the ionization potentials lie within a relatively small range (±1–2 eV), the band position is linearly related to I_D, as in eq 2. Equation 2 is obeyed by complexes involving trinitrofluorenone, tetracyanoethylene, and iodine as acceptors and a series of substituted benzenes as donors.[19]

$$h\nu_{CT} = -mI_D + b \tag{2}$$

Turning our attention to the molecular complexes of the arsines and triphenylphosphine with TCNE, the data in Table II clearly indicate that the band position energy ordering is $(C_6H_5)_3P > (C_6H_5)_3As >$ diarsine, with differences of at least 1000 cm^{-1} in each case. Because the same acceptor is used for all the charge-transfer complexes, the band position energy ordering should vary in the same way as the ionization potential of the donor. Thus, the I_D ordering should be $(C_6H_5)_3P > (C_6H_5)_3As >$ diarsine, which is in accord with a simple prediction based on the relative energies of arsenic and phosphorus lone-pair electrons and the inductive effects of aryl and alkl groups on electron-donor properties.

Voigt and Reid have correlated the position of the charge-transfer absorption with the ionization potential of the donor for a number of molecular complexes involving TCNE as acceptor.[20] For substituted benzene molecules as donors, values of $m = 0.83$ and $b = 4.42$ were reported for the parameters of eq 2. Using these values, and the lowest energy charge-transfer band from the spectra in Table II, we obtain the following I_D values: $(C_6H_5)_3P$, 8.30 eV; $(C_6H_5)_3As$, 8.15 eV; diarsine, 7.90 eV. These values for $(C_6H_5)_3Q$ are within 1 eV of the ionization potentials determined by standard techniques,[9] which is satisfactory agreement considering the assumptions made.

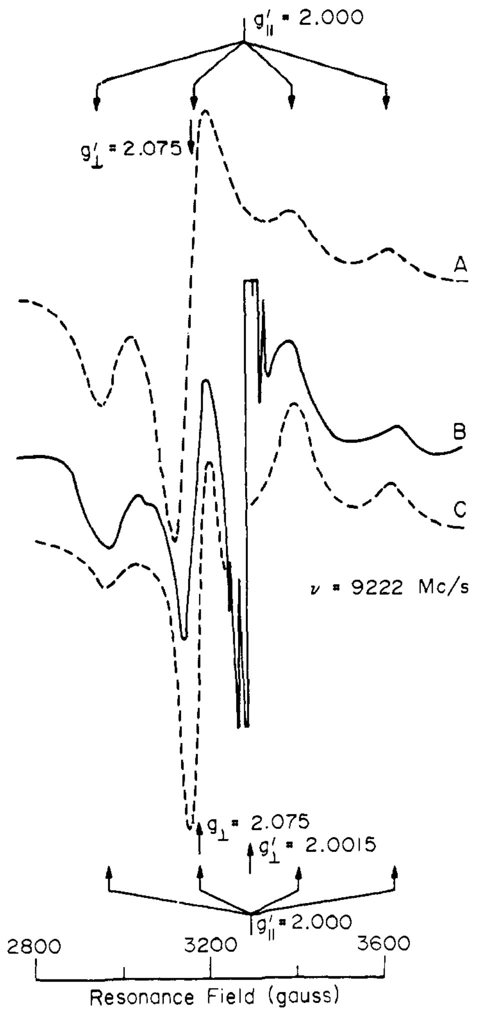

Figure 5. Observed (B) and simulated esr spectra of uv-irradiated $(CH_3)_2AsI$ in ethanol (96°K). Two simulated spectra are shown: spectrum A is based only on the species $[(CH_3)_2\ddot{A}s\cdot]$; spectrum C is based on a 3:50 ratio of $[(CH_3)_2AsI]^+$ and $[(CH_3)_2\ddot{A}s\cdot]$.

The ordering of ionization potentials is of course the reverse of the one-electron energies of the highest filled orbitals in the electronic structural scheme for the molecules; here we have diarsine $> (C_6H_5)_3As > (C_6H_5)_3P$. A comparison of the charge-transfer band positions with that of the (TCNE·toluene) complex ($\bar{\nu}_{max}$ 24,600 cm^{-1})[8] indicates that the lowest energy band in the spectrum of the TCNE–arsine or –phosphine complex must be due to charge transfer from the unshared pair on the heavy-donor atom, rather than from the aromatic π orbitals. On the basis of the relative energy positions of the n(As) or n(P) level in the arsines and phosphine, we might naively expect the position of the n → π^* transition in the arsine or phosphine alone to appear as the lowest energy band in the electronic absorption spectrum and to vary in the order diarsine $> (C_6H_5)_3As > (C_6H_5)P$. This transition in fact does not

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(14) W. R. Cullen, *Advan. Organometal. Chem.*, 4, 145 (1966).

(15) H. McConnell, J. S. Ham, and J. R. Platt, *J. Chem. Phys.*, 21, 66 (1953).

(16) H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 71, 2703 (1949).

(17) R. S. Mulliken, *ibid.*, 74, 811 (1952).

(18) G. Briegleb, "Elektronen-Donator-Acceptor Komplexes," Springer-Verlag, Berlin, 1961.

(19) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964.

(20) E. M. Voigt and C. Reid, *J. Amer. Chem. Soc.*, 86, 3930 (1964).

give rise to the lowest energy band in the electronic spectra of these molecules, and the observed energy ordering is $(C_6H_5)_3P > (C_6H_5)_3As \sim$ diarsine. It is apparent that interelectronic repulsion effects become the dominant factor in determining band position orderings within the spectrum of each molecule, reversing the ordering predicted on the basis of a simple one-electron energy level picture.

It was noted that the electronic spectra of the charge-transfer complexes exhibit *two* bands which do not appear in the spectra of the isolated components. A similar effect has been reported for charge-transfer complexes involving substituted benzene donor molecules.[20] This effect was first interpreted by Orgel[21] as due to a splitting in the charge-transfer excited state due to the presence of the substituent(s) on the benzene ring. For the complexes under consideration here, we suggest that the two charge-transfer transitions involve the two types of donor orbitals. The transition responsible for the lower energy band originates in the arsenic or phosphorus lone-pair orbital, whereas the higher energy transition involves the highest filled aromatic π orbital. The position of the charge-transfer absorption in the TCNE–benzene complex is 25,800 cm^{-1}, and in the toluene complex it is 24,600 cm^{-1}; these data are in quite reasonable agreement with the positions recorded in Table II for the second band in the TCNE–arsine and –phosphine complexes.

Electronic Structures of Arsine Radicals. First, we shall summarize briefly the proposed assignments of the esr spectra. In the spectrum of uv-irradiated diarsine, we have assigned the strong signal at $g = 2.075$ with seven hyperfine lines to the species (diars)$^+$. The seven-line pattern shown in the computer-simulated spectrum is in agreement with this assignment. The highly split pattern around $g = 2.00$ is assigned to one or more of the solvent-fragment radicals previously described. The other signals designated as g' ($g_{\parallel}' = 2.000$ and $g_{\perp}' = 2.0015$) in the simulated spectra are assigned to arsenic-containing fragments of the type $(R_2\ddot{A}s\cdot)$. Spectra of the other uv-irradiated arsines have been assigned in an analogous manner, the main difference being that $[(C_6H_5)_2AsCH_2]_2^+$ and $[(C_6H_5)_3As]^+$ appear to exhibit rhombic g tensors. The esr spectrum of uv-irradiated dimethyliodoarsine is essentially the same as that of diarsine, with the exception that hyperfine splitting was not observed on the signal arising from the molecular cation. The variation in the relative intensities of the molecular cation/$(R_2\ddot{A}s\cdot)$ signals observed in the several uv-irradiated arsines lends further support to our interpretation that these signals arise from both the molecular cation and $(R_2\ddot{A}s\cdot)$ radical, rather than from the $(R_2\ddot{A}s\cdot)$ species alone.

The ^{75}As hyperfine splitting parameters given in Table II may be used to estimate the 4s and 4p contributions to the orbital bearing the unpaired electron in the speices $(R_2\ddot{A}s\cdot)$. Taking as a reference point the calculated, one-electron 4s-isotropic and 4p-anisotropic arsenic splittings given by Lin and McDowell,[22] we estimate that the unpaired electron in $(R_2\ddot{A}s\cdot)$ is primarily 4p(As), being 2.2% 4s(As) and 77.6% 4p(As). The valence s–p hybridization in $(R_2\ddot{A}s\cdot)$ apparently is closely similar to that in $(\cdot\ddot{P}H_2)$, where an esr analysis yielded[23] 2.2% 3s(P) character in the half-filled orbital.

Perhaps of greatest importance is the comparison afforded by the optical spectral and esr data of the electronic structures of diarsine and (diars)$^+$. The electronic absorption spectrum of the (diars·TCNE) complex shows that the two highest occupied levels of diarsine are in an arsenic nonbonding orbital and a π molecular orbital confined to the aromatic ring. The latter conclusion is also supported by the fact that the $\pi \rightarrow \pi^*$ transition in diarsine is not substantially different in energy than in benzene itself. If we naively assume that the orbitals in (diars)$^+$ are the same as in diarsine, then the unpaired spin in the radical cation is expected to be localized in a level of primarily arsenic-orbital character. The C–As–C bond angles in $(CH_3)_3As$ and $(C_6H_5)_3As$ are 96°,[14] and the H–As–H angle in AsH_3 is 92°.[24] These bond angle data have been interpreted as an indication that the bonding in arsines involves essentially the 4p arsenic orbitals, and therefore that the lone pair resides primarily in 4s(As).[24] However, the ^{75}As hyperfine splitting parameters allow us to estimate that the half-filled molecular orbital in (diars)$^+$ is at most 0.13% 4s(As).

The esr data may be accommodated if we assume that there is a change in the geometrical arrangement of groups around arsenic in going from diarsine to (diars)$^+$. Removing one electron from an arsenic orbital decreases (bonded-pair)–(lone-pair) interelectronic repulsion effects and the C–As–C bond angles should increase. As a result, strong mixing between 4pπ(As) and aromatic ring π orbitals would be probable in the more nearly planar $[AsC_3]$ structure in (diars)$^+$. Thus in strong contrast to the situation in diarsine, the highest occupied level would be thoroughly delocalized over the entire π orbital network of (diars)$^+$. Our estimate that the unpaired electron is no more than 7.6% 4p(As) is consistent with this interpretation.

A delocalized unpaired-electron model is also compatible with the esr results for the radical cations $[(C_6H_5)_3As]^+$, $[(C_6H_5)_2AsCH_2]_2^+$, and $[(CH_3)_2AsI]^+$. In the latter case, 5p(I) and 4p(As) orbitals would be expected to mix strongly.

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