On the Use of Photoelectron Spectroscopy in Studying Rotational Isomerism in Tetramethyldiphosphine[1]

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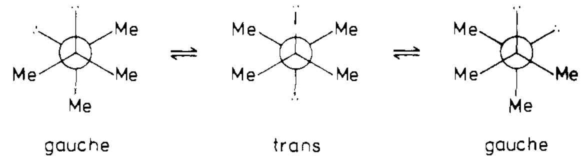
Abstract: Using variable temperature photoelectron spectroscopy (VTPES), angular dependent photoelectron spectroscopy (ADPES), and the Gaussian simulation technique of photoelectron spectra (GSPES) a new assignment of the UV photoelectron spectrum of tetramethyldiphosphine is derived and the equilibrium between its trans and gauche forms is quantitatively studied. The assignment is the same as those of similar hydrazines. The trans isomer is more stable than the gauche by 0.5 ± 0.1 kcal/mol meaning that the populations of each isomer are 60 and 40% at room temperature, respectively, and 50% each at 170 °C. These results do not confirm the interpretation of electron diffraction data.

Introduction

Various studies[2-6] on tetramethyldiphosphine in the gas phase agree that this compound is an equilibrium mixture of gauche and trans isomers. The derived populations, however, disagree: 100% of a near trans form at 170 °C according to an electron diffraction study,[3] 40% trans and 60% gauche from Raman data at ambient temperature,[2,4] and 84% trans and 16% gauche from a photoelectron spectral study at room temperature.[5] Additionally, two different assignments[5,6] of the photoelectron bands have been proposed.



Based on variable temperature photoelectron spectroscopy[7] (VTPES), angular dependent photoelectron spectroscopy[8] (ADPES), and Gaussian simulation of photoelectron spectra[9] (GSPES) evidence will be presented that the trans and gauche populations are about 60 and 40%, respectively at room temperature and about 50% each at 170 °C. Moreover, it will be shown that both previous photoelectron spectral assignments[5,6] must be abandoned in favor of an assignment which is analogous to the one made for similar hydrazines.[10]

Experimental Section

The photoelectron spectra at varying temperatures were recorded on a modified Perkin-Elmer PS 16 spectrometer equipped with a heated target chamber[7a] and a M 6800 Motorola microprocessor.[7c] Heating is accomplished by a bifilar stainless steel electric heater and the sample temperature is measured by a thermocouple inserted in the gas stream. The processor controls the voltages of the analyzer and accepts and counts the electron pulses prior to passing them to the computer memory. Each spectrum consists of 1024 data points (channels), averaged over 128 single scans, with 32 ms sample time at each point. The spectra are calibrated with xenon. For all temperatures applied, the spectral resolution as well as the calibrations was checked. In all cases the resolution $E/\Delta E$ was about 220 corresponding to a half-width of the argon signal of 25 meV. For each temperature used three spectra were taken.

The digitalized spectra were also processed on the TR 440 computer to achieve a Gaussian simulation of the spectra according to a modified[11] Levenberg method.[12]

In order to exclude decomposition products (produced by pyrolysis) a series of spectra were taken using the following instrumental setup. Two identical heated target chambers, one mounted externally and heated to the various temperatures and the other inserted into the spectrometer and maintained at room temperature, were connected by a sufficiently long tube to allow cooling of the sample vapor to room temperature.

The angular dependent photoelectron spectra were recorded on a Vacuum Generators ADES 400 spectrometer connected to the aforementioned microprocessor system. The pass energy of the analyzer was set to 5 eV. The processor then controlled the retarding voltage of the analyzer, counted the electron pulses, and passed them to the computer memory. Each spectrum consisted of 512 data points, averaged over 256 single scans, with 32 ms sample time at each point. The digitalized photoelectron spectra at various angles were further processed on the TR 440 computer to derive the asymmetry parameter over the spectrum.[13]

The tetramethyldiphosphine was prepared according to the method of Parshall[14] and carefully handled under argon. The spectrometers were flashed with ammonia before letting the diphosphine in. In spite of all these precautions it took about 1 h until the spectra assume their final reproducible form, showing that small amounts of byproducts are unavoidable with the synthetic and purification procedures. After these impurities were eliminated in the high vacuum of the spectrometers, reproducible photoelectron spectra could be produced for weeks, as long as the internal parts of the spectrometers were protected from contact with the air.

Results and Discussion

Pyrolysis Experiments. We first determined the temperature range over which tetramethyldiphosphine is chemically stable under the experimental conditions of photoelectron spectroscopy. Using the experimental setup described in the preceding section we recorded the usual room temperature spectrum (e.g., the spectrum of Figure 1) up to a pyrolysis temperature of about 260 °C. At higher temperatures the intensity of band 3 sharply increases probably owing to lone pair ionization (occurring at 8.58[15a] and 8.60 eV[15b]) of trimethylphosphine, a decomposition product. Figure 2 displays the relative peak heights h_4/h_3, h_1/h_3, and h_4/h_t as a function of pyrolysis temperature as well as the peak heights ratio h_4/h_3 obtained as a function of temperatures applied in the variable temperature photoelectron spectral (VTPES) measurements described below. The results clearly show that tetramethyldiphosphine does not decompose below 260 °C so that the VTPES changes detected must be due to molecular changes different from decomposition. Below we interpret these changes as due to rotational isomerism.

Variable Temperature Photoelectron Spectral (VTPES) Measurements. Figure 3 presents the photoelectron spectra at various temperatures below 260 °C. The most prominent changes that occur with increasing temperature are broadening of band 1 and increasing intensity of band 3 relative to bands 1 and 4.

Two preceding photoelectron spectral studies[5,6] agree in assigning bands 1 and 4 to the n_- and n_+ ionizations of *trans*-tetramethyldiphosphine but are at variance with the assignments of the corresponding lone pair ionizations of the gauche form. Cowley, Dewar, et al.[5] presume both the n_- and

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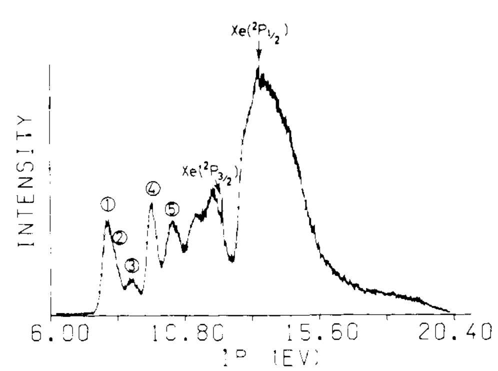

Figure 1. Photoelectron spectrum of tetramethyldiphosphine.

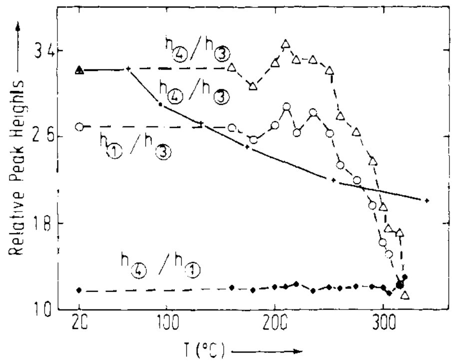

Figure 2. Relative peak heights in the photoelectron spectra of tetramethyldiphosphine taken at room temperature after pyrolysis as a function of pyrolysis temperature (dashed lines) and taken at various temperatures in the heated target chamber when applying the VTPES technique (solid line).

n+ ionizations under the envelope of band 3 while Turner et al.[6] consider band 3 to be due to the n− ionization, with the n+ ionization hidden under the envelope of band 4.

Assuming the trans form to be more stable than the gauche form (in accordance with the photoelectron spectrum at room temperature) the intensities of bands originating from the gauche form are expected to rise at higher temperatures and the ones due to ionizations from the trans isomer to decrease. In view of this, our VTPES results do not corroborate the assignment of Turner et al.[6] Moreover, the marked broadening of band 1 (not occurring for band 4) suggests a third (besides the assignments of Cowley, Dewar, et al.[5]) way of assigning the spectral features, namely, that band 3 is due to the n+ ionization of the gauche form and that the corresponding n− ionization is hidden under the high-energy side of band 1. This third assignment proposal is analogous to the assignment made by Nelsen et al.[10] in similar hydrazine cases.

Unfortunately, the spectral changes brought about by the VTPES technique (shown in Figure 3) are insufficient for the correct determination of band structure (i.e., either two ionizations under band 1 and one under band 3 or conversely[5]) by themselves. Therefore attempts were made to measure the angular dependence of the photoelectron spectrum of tetramethyldiphosphine and to analyze the variable temperature photoelectron spectra by a Gaussian simulation technique.

Angular Dependent Photoelectron Spectral (ADPES) Measurements. This technique consists of observing the photoelectron spectrum as a function of the angle Θ between the direction of the photon beam and outgoing electron. Each ionization band will have a characteristic angular distribution given in terms of a parameter β. By determining β over the whole spectrum one can untangle the different electron bands.[8]

Because of experimental limitations (sensitivity of the ADES 400 machine, low intensity of the lone pair ionization of tetramethyldiphosphine, as well as contamination problems) we could only record photoelectron spectra at two different angles (Θ = 90 and 150°) and the spectra were rather noisy. For that reason they were smoothed using 23 point polynomials.[16] As a consequence the β curve turns out to be noisy too, but, nonetheless, significant. This curve along with the 90° spectrum is shown in Figure 4.

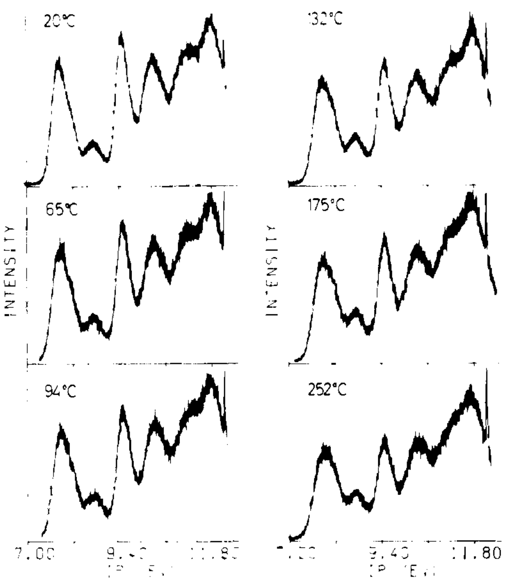

Figure 3. Photoelectron spectra of tetramethyldiphosphine at six selected temperatures (20, 65, 94, 132, 175, and 252 °C).

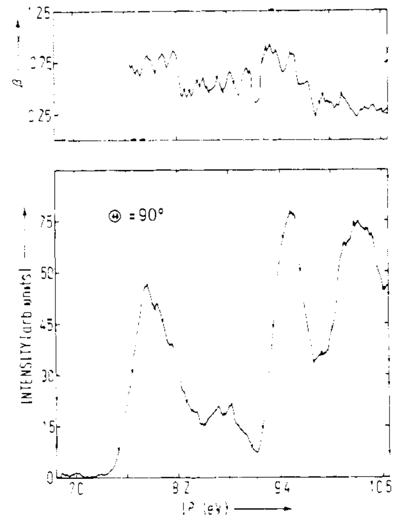

Figure 4. Photoelectron spectrum of tetramethyldiphosphine taken at Θ = 90° with the ADES 400 spectrometer. The upper part of the figure gives the angular parameter β as a function of the spectrum.

From the β curve we see that most of the first band (beginning on the low-energy side) as well as of the band 4 (again beginning on the low-energy side) is characterized by a β value of about 0.7. This means that the n− and n+ ionizations of the trans form have equal β values. Furthermore, for most of the portion of band 3 a β value of about 0.5 is obtained. However, it is most interesting that the latter range (with β = 0.5) extends rather far into the region of band 1. According to these results it is very likely that the n− ionization of the gauche form is hidden under the high-energy side of band 1 and that consequently band 3 arises from the n+ ionization of the gauche form only. This result gets nice support from an application of the Gaussian simulation technique.

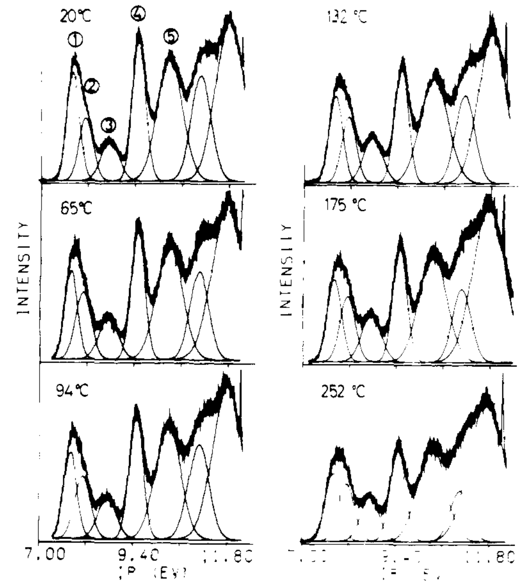

Figure 5. Gaussian curve fitting of photoelectron spectra of tetramethyldiphosphine at six selected temperatures (20, 65, 94, 132, 175, and 252 °C).

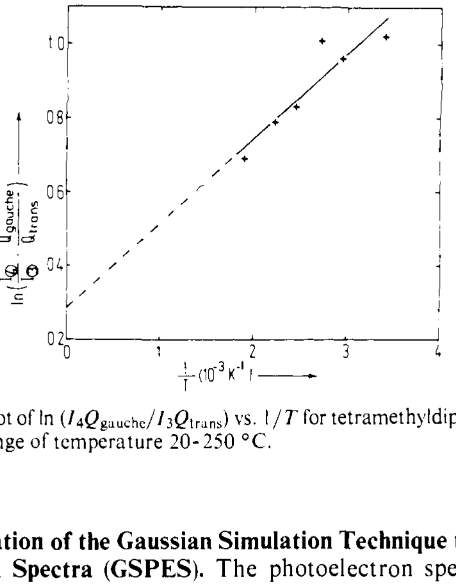

Figure 6. Plot of $\ln(I_4Q_{\text{gauche}}/I_3Q_{\text{trans}})$ vs. $1/T$ for tetramethyldiphosphine over the range of temperature 20–250 °C.

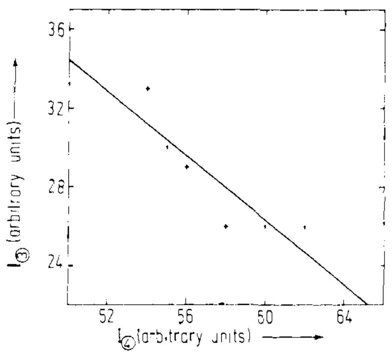

Figure 7. Plot of I_3 vs. I_4 for tetramethyldiphosphine over the range of temperature 20–250 °C.

Application of the Gaussian Simulation Technique to Photoelectron Spectra (GSPES). The photoelectron spectra at various temperatures (cf. Figure 3) are Gaussian fitted over the range of 7–12.5 eV using seven symmetrical Gaussian functions. Each Gaussian band is determined by three parameters: its position (i.e., the ionization potential of the maximum), its peak height, and its half-width. The resulting 21 parameters are determined in a nonlinear least-squares fit to the spectral trace. Background was simulated by a base line with height being determined by the count rate prior to the first spectral band. This parameter was kept fixed.

We tried two models: two Gaussian bands were placed either under the envelope of band 3 according to the interpretation of Dewar, Cowley, et al.[5] or under the envelope of band 1 according to the proposal of the present work. Irrespective of these different starting conditions it turned out that, in all cases and for all temperatures, the final result of the fit (Figure 5) was two Gaussian bands under band 1. Quantitatively, we obtained for the ionization potentials in eV (standard deviation) using the assignments of Cowley, Dewar, et al., 7.81 (±0.02), 8.14 (±0.03), 8.76 (±0.01), 9.49 (±0.01), 10.31 (±0.03). These values are in excellent agreement with the present investigation which yields ionization potentials of 7.80 (±0.02), 8.13 (±0.03), 8.75 (±0.01), 9.48 (±0.01), 10.31 (±0.02).

Relying on these and the ADPES results we now conclude that band 1 consists of two overlapping bands with one much more intense than the other. Hereafter, we refer to these bands as bands 1 and 2. We then assign the first five bands as follows: 1, 7.80 eV/$n_{-,\text{trans}}$; 2, 8.13 eV/$n_{-,\text{gauche}}$; 3, 8.75 eV/$n_{+,\text{gauche}}$; 4, 9.48 eV/$n_{+,\text{trans}}$; and 5, 10.31 eV/σ_{pp}.

Quantitative Analysis of Photoelectron Intensities. The intensity of a photoelectron band is given as[17]

$$I = I^* l n \frac{\sigma}{4\pi}\left[1 + \frac{\beta}{2}\left(\frac{3}{2}\sin^2\Theta - 1\right)\right] \qquad (1)$$

I^*, l, n, σ, β, and Θ are the light intensity, the length of the ionization region, the particle density, the total ionization cross section, the asymmetry parameter, and Θ as defined above, respectively. Based on eq 1 the relative intensity of, say, bands 4 to 3 at $\Theta = 90°$ is

$$\frac{I_4}{I_3} = \frac{n_{\text{trans}}}{n_{\text{gauche}}}\,\frac{\sigma_{n+,\text{trans}}}{\sigma_{n+,\text{gauche}}}\,\frac{1 + \frac{\beta_{n+,\text{trans}}}{4}}{1 + \frac{\beta_{n+,\text{gauche}}}{4}} \qquad (2)$$

Introducing the equilibrium constant K through

$$K = \frac{n_{\text{trans}}}{n_{\text{gauche}}} = \frac{g_{\text{trans}}}{g_{\text{gauche}}}\,\frac{Q_{\text{trans}}}{Q_{\text{gauche}}}\exp\left(-\frac{\Delta E}{RT}\right) \qquad (3)$$

where $g_{\text{trans}}/g_{\text{gauche}}$ is the ratio of statistical weights of both conformers, $Q_{\text{trans}}/Q_{\text{gauche}}$ the ratio of partition functions, and ΔE the difference in total bonding and vibrational energy between them with R and T having their usual meaning, we finally arrive at

$$\ln\left[\frac{I_4}{I_3}\,\frac{Q_{\text{gauche}}}{Q_{\text{trans}}}\right] = -\frac{\Delta E}{RT} + \ln A \qquad (4)$$

with

$$A = \frac{\sigma_{n+,\text{trans}}}{\sigma_{n+,\text{gauche}}}\,\frac{g_{\text{trans}}}{g_{\text{gauche}}}\,\frac{1 + \frac{\beta_{n+,\text{trans}}}{4}}{1 + \frac{\beta_{n+,\text{gauche}}}{4}} \qquad (5)$$

The asymmetry parameters β_{n_+} for the trans and gauche form are known (see above). $g_{\text{trans}}/g_{\text{gauche}}$ equals ½. The relative intensities I_4/I_3 were determined from the areas of the Gaussian bands. They are (for the temperatures applied) 2.4 (20 °C), 2.2 (65 °C), 2.3 (94 °C), 1.9 (132 °C), 1.8 (175 °C), 1.6 (252 °C). The relative partition functions $Q_{\text{gauche}}/Q_{\text{trans}}$ were calculated using standard formulas of statistical thermodynamics and molecular data contained in the literature (vibrational frequencies of ref 2 and 4 and geometrical data of ref 3) with the additional assumptions that the azimuthal angles between the two lone pairs are 60 and 180° for the gauche and trans forms, respectively, and that all other geometrical data do not vary as a function of the azimuthal angle. The values of $Q_{\text{gauche}}/Q_{\text{trans}}$ obtained are 1.14 (20 °C), 1.17 (65 °C), 1.18 (94 °C), 1.18 (132 °C), 1.20 (175 °C), and 1.22 (252 °C). From a plot of ln $(I_4 Q_{\text{gauche}}/I_3 Q_{\text{trans}})$ vs. $1/T$ (Figure 6) we estimate $\Delta E = -0.5 \pm 0.1$ kcal/mol and $\sigma_{\text{n+,trans}}/\sigma_{\text{n+,gauche}} = 2.5 \pm 0.4$. Accordingly, the trans form is more stable than the gauche form by 0.5 kcal/mol.

However, the ratio of cross sections found in this way is unrealistically high showing that the linear extrapolation to infinitely high temperature is not quite appropriate. The correct value of $\sigma_{\text{n+,trans}}/\sigma_{\text{n+,gauche}}$ can be easily obtained to be 1.2 ± 0.2 from a plot of I_3 vs. I_4 (Figure 7) according to

$$I_3 = \text{const} - \frac{\text{n}_{+,\text{gauche}}}{\text{n}_{+,\text{trans}}} \frac{1 + \dfrac{\beta_{\text{n+,gauche}}}{4}}{1 + \dfrac{\beta_{\text{n+,trans}}}{4}} I_4 \qquad (6)$$

Equation 6 follows from the fact that the total particle density equals the sum of n_{gauche} and n_{trans} for the various temperatures used. The particle density is kept constant during the measurements as well as the incident light intensity.

After $\Delta E = -0.5$ kcal/mol, $g_{\text{trans}}/g_{\text{gauche}} = 1/2$, and the respective values of $Q_{\text{trans}}/Q_{\text{gauche}}$ were inserted into eq 3 the populations mentioned in the Introduction were obtained.

Conclusion

The present investigation demonstrates that advanced photoelectron spectral techniques (VTPES, ADPES, and GSPES) are of considerable help in solving the rather complicated problem of rotational isomerism in tetramethyldiphosphine. In this way, it is established that the prevailing trans conformer (at room temperature) is more stable than the gauche isomer by 0.5 kcal/mol. Accordingly, at 170 °C there is 50% of the trans form as well as the gauche form. This result disagrees with the result of electron diffraction showing again[7d] that this technique might lead to considerable misinterpretation. From a photoelectron spectral standpoint it is gratifying to note that the lone pair band pattern of a mixture of gauche and trans isomers turns out to be just the same as in similar hydrazine cases.

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Relatively Stable Silaethylenes. Photolysis of Acylpolysilanes

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Abstract: The syntheses of a variety of acyldi- and acylpolysilanes are described. All of these when photolyzed at about λ 360 nm give rise to silaethylenes, as evidenced by trapping experiments with methanol, a diene or an alkyne. In the absence of trapping agents the silaethylenes undergo head to head dimerization to 1,2-disilacyclobutanes. Of the various silaethylenes, the one produced from pivaloyltris(trimethylsilyl)silane is found to have a moderate lifetime at room temperature, and to be in a mobile equilibrium with its dimer. The silaethylene and its dimer have been characterized by UV, ^{1}H NMR, and ^{13}C NMR spectra. Thermolysis of the pivaloylsilane in the presence of alcohols, or phenylpropyne, also gave the products resulting from trapping of the silaethylene.

The pioneering work of Gusel'nikov and Flowers unambiguously demonstrated for the first time the intermediacy of reactive species containing silicon–carbon double bonds (silaethylenes) during the thermolysis of silacyclobutanes.[1] During the succeeding years a multitude of systems have been described which under thermolysis or photolysis conditions appear to give rise to short-lived silaethylenes, as demonstrated by various trapping experiments.[2]

Our entry into this field came as a logical consequence of our studies on acylsilanes[3,4] and β-ketosilanes,[5] both of which we had shown readily underwent either photochemical or thermal rearrangements. Acylsilanes, using radiation in the

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