transfer of triplet excitation from solvent to solute; other models for excitation transfer can be adapted to fit the kinetic observations but seem over-all to be less attractive to us at this time.

Experimental Section

Materials. Samples of purified *trans*- and *cis*-1,2-diphenylpropene were generously supplied to us by Professor D. J. Cram and Dr. D. H. Hunter and were used without further purification. The purification of the stilbenes used in this work has been described.[10] *trans*-Piperylene was obtained from technical grade piperylene by preparative vapor phase chromatography. Reagent grade benzene proved sufficiently pure for these studies.

Radiolyses. Solutions (1-4 ml) of the appropriate substrate in benzene were prepared, degassed, and irradiated in sealed Pyrex 13 × 100 mm tubes. Some initial experiments were performed on undegassed samples with little difference in short-term runs with concentrations of scavengers greater than 0.02 *M*. Irradiations were carried out in a Co^{60} cavity source.[23] Dosimetry (Fricke, $G =$ 15.5) was carried out in similar Pyrex tubes, open to the air. The dose rate (corrected for absorption by the organic solvent and solute) was approximately 2.7×10^{19} ev g^{-1} hr^{-1}. Conversions in the *cis-trans* isomeric systems were carried to 5-50% of completion. Stationary states were usually obtained after irradiating dilute (*ca.* 0.02 *M*) solutions until a total dose of $3\text{-}6 \times 10^{21}$ ev (120-hr duration) had been absorbed.

Analyses were performed by vapor phase chromatography. An internal standard was added to the sample after irradiation, and measurement of relative peak areas gave the amount of each solute present after irradiation, when the usual detector response correction was made.

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(23) We are indebted to Dr. James King and The National Aeronautics and Space Administration for the use of the source at the Jet Propulsion Laboratory, Pasadena, Calif.

The Structure of the Solvent Shells of Electrons.
I. Hexamethylphosphoramide

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Abstract: Electrons are solvated by hexamethylphosphoramide in such a way that there are four equivalent nearest neighbor solvent molecules, tetrahedrally arranged, with P^{31} contact hyperfine splittings of 4.91 gauss and six next-nearest neighbor solvent molecules, octahedrally arranged, with P^{31} splittings of 1.83 gauss. All of the 35 lines of the epr spectrum to be predicted for such a ten-molecule complex have been found, in the expected intensity ratios. The *g* value, line widths, and splittings of the solvated electron spectrum are independent of the cation, Li^+, Na^+, or K^+, present in the solution. At high concentrations of alkali metals, other unidentified paramagnetic species predominate in the solution.

Alkali metals dissolve or appear to dissolve in a variety of liquids of high dielectric constant such as ammonia, amines, or ethers to give blue solutions. In the case of the ethers dimethoxyethane and tetrahydrofuran, the blue solutions of potassium were found to be diamagnetic.[1] In the better known case of metal-ammonia solutions, strong epr signals are obtained.[2] Pollak[3] showed that the electron relaxation times are longer in $N^{15}H_3$ solutions than in $N^{14}H_3$ solutions. This is indirect evidence of a weak contact hyperfine interaction of the unpaired electron with the nitrogen nuclei of the solvent molecules surrounding the electron.

In 1961 G. Stork and D. R. Coulson at Columbia University observed the blue color of solutions of alkali metals in hexamethylphosphoramide [tris(dimethylamino)phosphine oxide], $([CH_3]_2N)_3PO$, and it was suggested that we make an epr study of these solutions. Subsequently a single epr signal was detected in these solutions.[4]

Experimental Section

The conventional Varian V-4500 X-band epr spectrometer was used, with a V-4013A magnet suitable for high-resolution nmr experiments. When necessary the field was modulated at 400 Hz, as well as 100 kHz, to rule out possible modulation side bands. The hexamethylphosphoramide was obtained distilled from Dow Chemical Co. The solutions were degassed by repeated freezing and evacuation at 10^{-5} mm and lower.

Line intensities were determined from the derivative of the absorption spectrum by utilizing the relation

$$\int_{-\infty}^{\infty} f(B)\,dB = \left|\int_{-\infty}^{\infty} Bf'(B)\,dB\right| \qquad (1)$$

where B is the difference in gauss between the field value and the center of the line, and $f'(B)$ is the ordinate of the recorder trace. A typical line was subdivided into 20 or more parts, and the quantity $Bf'(B)$ was summed over all of the line visible above the noise.

Magnetic fields were measured by the proton magnetic resonance method, using a Hewlett-Packard 5245L counter. The microwave

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(1) F. S. Dainton, D. M. Wiles, and H. N. Wright, *J. Chem. Soc.*, 4283 (1960); F. A. Cafasso and B. R. Sundheim, *J. Chem. Phys.*, **31**, 809 (1959).

(2) C. H. Hutchison and R. C. Pastor, *ibid.*, **21**, 1959 (1953); T. P. Das, *Advan. Chem. Phys.*, **4**, 303 (1962).

(3) V. L. Pollak, *J. Chem. Phys.*, **34**, 864 (1961).

(4) G. Fraenkel, S. H. Ellis, and D. T. Dix, *J. Am. Chem. Soc.*, **87**, 1406 (1965).

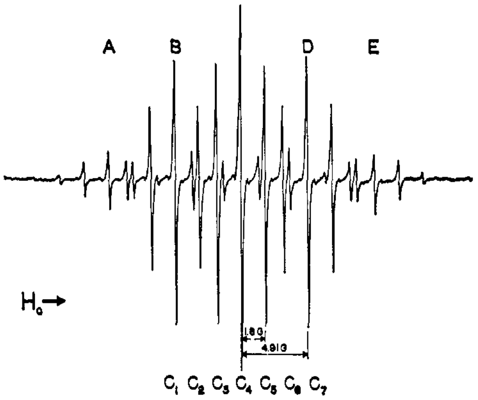

Figure 1. Epr spectrum of solvated electrons in hexamethylphosphoramide.

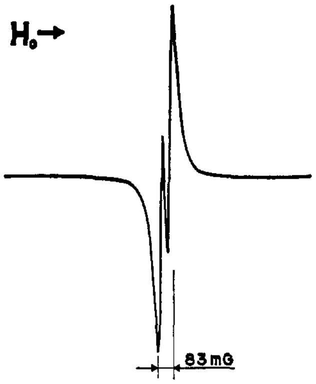

Figure 2. Epr spectrum of the species predominating at high concentrations of alkali metals in phosphoramide.

frequency was measured with the same counter just before and just after field measurements, and an average of the two measurements was used for g value calculations. Usually the drift in klystron frequency was negligible. To calibrate our g value measurement apparatus and procedures, we have measured the g values of the benzosemiquinone anion in ethanol and 1,1-diphenylpicrylhydrazyl in benzene. We found them to be 2.00465 and 2.00349, respectively, in good agreement with very accurate published results of 2.00468 and 2.00354.[5]

Results

In dilute solutions, *i.e.*, 0.01 to 0.001 M of Li or Na, a blue solid phase was observed which tends to settle. Except where stated, the epr observations were made on the clear supernatant liquid of these dilute solutions. Concentrated solutions are completely blue, with no apparent settling tendency.

A characteristic 35-line spectrum is observed in all these solutions (Figure 1). The g value is 2.0027 ± 0.0001. Five groups of seven lines each are present, the groups being separated by a hyperfine splitting of 4.91 ± 0.02 gauss. The intensity ratios of the five groups as measured were 1:4.08:5.97:4.15:1. In Figure 1 the lines marked A, B, C_4, D, and E are the central lines of each group. The seven lines of the central group are labeled as C_1 to C_7. The intensity ratios of the lines C_1 to C_7 were 0.94:6.00:16.86:25.2:15.54:6.00:0.94. Similar ratios were obtained in the other smaller groups, wherever the line intensity was sufficiently greater than the noise to make meaningful measurements. The smaller hyperfine splitting inside of each of these five groups is 1.83 ± 0.02 gauss. The widths of these 35 lines are all about 105 mgauss. The lines are somewhat asymmetric. This asymmetry was markedly increased if more microwave power than 1 mw was used. These same hyperfine splittings, line width, and the same g value were found no matter whether lithium, sodium, or potassium was used.

As the concentration of alkali metal was raised, the 35-line spectrum broadened, eventually to indetectability. As the spectrum broadened, two new lines appeared. At high concentrations of alkali metal, only these two lines were seen (Figure 2). The g = 2.0023 ± 0.0001 position is halfway between these two overlapping lines. A line in this region has previously been reported.[4]

Solutions of potassium in hexamethylphosphoramide were different from those of sodium and lithium in that there was no evident tendency to precipitate a solid. It was necessary to wait for the chemical decay of most (but not necessarily all) of the strong signals near g = 2.0023 before the lines of the 35-line spectrum centered at g = 2.0027 became narrow enough to be detected.

Discussion

The principal causes of the deviation of the intensity ratios from small integers are the asymmetry of the lines, the weakness of the signals being measured, and excessive field modulation. The deviations were largest when the smallest lines were involved, because they have a relatively larger portion that is lost in the noise. Moreover, because of the 100-mgauss line width, the field modulation amplitude had to be almost as much as the line width. Consequently, a true derivative spectrum could not be obtained, and the use of eq 1 introduces an error. Nonetheless, the data are good enough to rule out the following *a priori* possibilities for the ratios of the seven lines in each group: 1:3:6:7:6:3:1, 1:4:7:8:7:4:1, and 1:5:11:14:11:5:1. This leaves 1:6:15:20:15:6:1 as by far the best for the theoretical intensity ratio. The experimental intensity ratios of the five groups A, B, C, D, and E are in excellent agreement with the theoretical intensity ratios 1:4:6:4:1. We conclude that there are present four equivalent nuclear spins of $^1/_2$ and six equivalent nuclear spins of $^1/_2$ with a somewhat smaller electron spin density than the four equivalent nuclei.

The epr evidence attesting to fourfold equivalence inside of a sixfold equivalence categorically rules out a square-planar structure. An equilibrium structure which is in complete agreement with this evidence is that of an electron bonded to four nearest neighbor solvent molecules, the four phosphorus atoms being tetrahedrally arranged and somewhat less strongly bonded to six next-nearest neighbors arranged in cubic fashion outside of the four inner molecules. The relation of the tetrahedron of oxygen atom to the tetrahedron of phosphorus atoms is not deducible from these data. Consequently, the correct structure may be either that of Figure 3 or that of Figure 4, or even an equilibrium mixture of the two. We have built models of both versions and find no excessive steric hindrance in either. In view of the absence of N^{14} splittings, the nuclei of spin $^1/_2$ are concluded on chemical grounds to be P^{31} nuclei.

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(5) M. S. Blois, Jr., H. W. Brown, and J. E. Maling, Ninth Colloque Ampere, Librairie Payot, Geneva, 1960, pp 243–255.

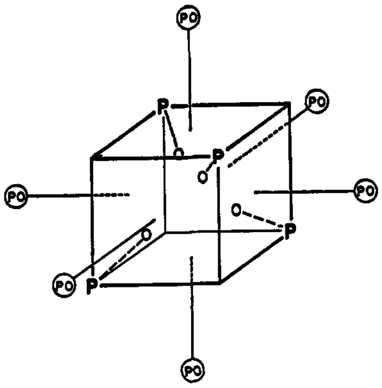

Figure 3. One possible arrangement of the ten solvent molecules solvating the unpaired electron. The four inner P–O bonds point toward a common center. The three dimethylamino groups of each molecule have been omitted from this sketch.

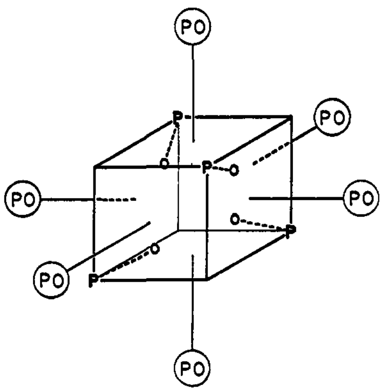

Figure 4. The other possible arrangement of the ten molecules solvating the electron. The four inner P–O bonds do not point toward a common center. The cube does not represent chemical bonding. It is drawn to give the reader a coordinate system.

Solvation in this system is accomplished by bonding of the unpaired electron to the ten solvent molecules. The unpaired electron density evaluated at the P^{31} nucleus, $|\Psi(0)|^2$, is 0.0513 electron/A^3 for the nearest neighbor P^{31} atoms and 0.01913 electron/A^3 for the next-nearest neighbor P^{31} atoms.[6] The total of these densities is 0.3199 A^{-3}. This is the same order of magnitude as the $|\Psi(0)|^2$ for P^{31} atoms in the gas phase which, from the contact hyperfine splitting of 19.65 gauss,[7] is seen to be 0.2055 A^{-3}. These are both cases of spin polarization of the core s electrons by the unpaired electron, whose orbital does not have appreciable s character. If the wave function of the unpaired electron did have appreciable s character, one would obtain a P^{31} splitting one or two orders of magnitude greater than that observed here. An example would be the 1347-gauss splitting found for PF_4.[8] The decrease of $|\Psi|^2$ from the inner shell to the second shell is gradual enough that it suggests that still another solvent shell may exist which has significant spin density. Presumably any outermost shell of bonding solvent molecules could not be detected in the epr spectrum because the molecules of this shell exchange too frequently with solvent molecules containing P^{31} nuclei of opposite spin. The number of detectable shells should be a function of temperature.

The strength of the bonding, *i.e.*, the general stability of this solvated electron system $(([CH_3]_2N)_3PO)_{10}^-$, is further shown by its lifetime. The line width of about 100 mgauss requires, by the uncertainty principle, a lifetime of at least several tenths of a microsecond for the system. The true lifetime may, of course, be far longer than this.[9]

The identity of the species or two species at g = 2.0023 is not clear. The available information does not rule out either a less elaborately solvated electron and/or radicals with spectral lines narrowed by electron transfer.

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(6) These electron densities are calculated by the use of the equation, $|\Psi(0)|^2 = \Delta B/({}^8/_3\pi g_I\mu_n)$, where ΔB is the hyperfine splitting in gauss, g_I is the nuclear g factor which is 2.261 for P^{31}, and μ_n is the nuclear magneton in erg/gauss. The equation is obtained by appropriate substitution and rearrangement from Fermi's equation, $\mathcal{A} = -{}^8/_8\pi g_I\cdot \mu_n g_e \mu_B|\Psi(0)|^2$, where $\mathcal{A}$ is the hyperfine splitting in ergs, g_e is the g value of the electron, and μ_B is the Bohr magneton in erg/gauss.

(7) R. H. Lambert and F. M. Pipkin, *Phys. Rev.*, **128**, 198 (1962).

(8) J. R. Morton, *Can. J. Phys.*, **41**, 706 (1962).

(9) We may observe parenthetically that because of the cubic symmetry the g factor must be isotropic; consequently, there can be no contribution to the line width from unaveraged g factor anisotropy.