

EPR studies of phosphine photofragments in cancrinite matrix at 77 K

P RAGHUNATHAN* and S K SUR

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

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Abstract. The far-UV photolysis of phosphine sorbed in cancrinite matrix at 77 K has been studied by EPR spectroscopy. Cancrinite is demonstrated to stabilise the photolytically generated radicals $\cdot\text{PH}_2$, $\cdot\text{P}$ and $\cdot\text{H}$. Computer simulation of the entire lineshapes has been employed to assess the spin Hamiltonian parameters for both $\cdot\text{PH}_2$ and $\cdot\text{P}$. The intensity distribution pattern of the $\cdot\text{PH}_2$ spectrum at 77 K is indicative of a thermally-equilibrated population of rotational states of this radical in its matrix environment. The similarity of the EPR data of $\cdot\text{PH}_2$ trapped in cancrinite to that isolated in rare gas matrices, as well as the isotropic nature of the ^{31}P and ^1H hyperfine couplings in the former situation, suggest that $\cdot\text{PH}_2$ is trapped in pseudospherical cavities of cancrinite with minimal matrix perturbations. Marked departures are observed for the g - and A - values of cancrinite-trapped P atoms as compared with the gasphase counterparts.

Keywords. Free radical; matrix interaction; far-UV photolysis; phosphine; cancrinite; computer simulation; CNDO/2 method; spin density; zeolite.

1. Introduction

The photolysis of group V hydrides, mostly in frozen matrices of rare gases, and the EPR study of the atomic and molecular free radical species produced thereby, has been an active area of research in the last two decades (Adrian *et al* 1962; Jackel and Gordy 1968; Jackel *et al* 1968; McDowell *et al* 1972). In particular, it is known that the photolysis of phosphine (PH_3) by γ -rays (Jackel and Gordy 1968; Jackel *et al* 1968; Colussi *et al* 1975) and far-UV (McDowell *et al* 1972) leads to photoreactions that could be both rich and complex. Further, noticeable interactions between the isolated radical and the surrounding trap, collectively called "matrix effects" (Adrian 1962), have been known to influence the geometry and spin-density distribution of various trapped paramagnetic species.

Most of the earlier investigations were carried out at very low temperatures where rigid matrix supports could be formed. Hence the present authors investigated the far-UV photolysis of PH_3 in a suitably rigid, higher temperature 'molecular sieve'. As a convenient choice, the aluminosilicate matrix of cancrinite ($\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24} \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$) was preferred, as this solid has a well-characterised zeolite framework with P6_3 space group symmetry and hollow enclosures (Zarchow 1965; Smith 1976). Polycrystalline synthetic cancrinite has been successfully employed as an efficient matrix 'host' for a variety of paramagnetic species (Raghunathan and Sur 1983; Sur 1982). This seems to be the first report of the photolysis of PH_3 in a zeolitic matrix.

*To whom correspondence should be addressed.

2. Experimental

The phosphine gas used was of research-grade ($\sim 99.5\%$ pure, Matheson Gas Products, Canada). The gas at a pressure of ~ 600 torr was sorbed in cancrinite which was previously activated in a vacuum line by conventional methods (Barrer *et al* 1968). The unadsorbed PH_3 was then pumped off at room temperature. The sealed sample tubes were maintained at 77 K inside the slotted reactangular X-band (9.47 GHz) EPR cavity of a Varian E109 spectrometer system and exposed to far-UV radiation from an Argon resonance lamp and the spectra were recorded.

3. Results and discussion

The EPR spectrum obtained at 77 K by far-UV photoirradiation of PH_3 sorbed in cancrinite is shown in figure 1. As indicated by the splitting pattern at the bottom of figure 1, the spectrum may be analysed as a composite of EPR lines from the $\cdot\text{PH}_2$ radical with a superimposed doublet spectrum from phosphorous atom. In addition, a much larger doublet hyperfine splitting also arises from the H atom, which is always produced in the phosphine photolysis process (McDowell *et al* 1972). This splitting, which was measured to be 503.5 gauss or 0.047 cm^{-1} apart, is not included in figure 1. The primary photolytic steps are thought to be the following:

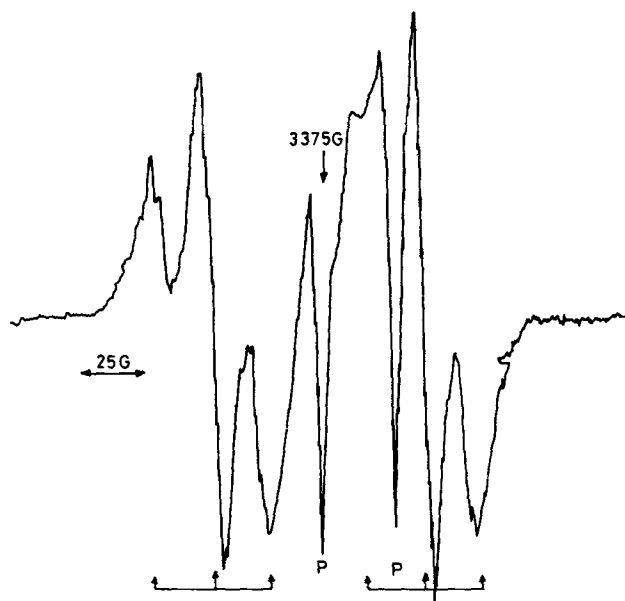
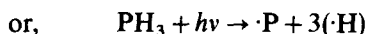
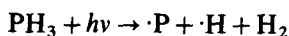
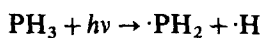


Figure 1. EPR spectrum of free-radicals formed by far-UV photo-irradiation of PH_3 in cancrinite matrix at 77 K (the 503 gauss wide outermost doublet due to H atom is not shown).

The resultant $\cdot\text{PH}_2$, $\cdot\text{P}$ and $\cdot\text{H}$ radicals subsequently become stabilised within the cancrinite host. This mechanism is also supported by results obtained in the earlier studies using rare gas matrices (Jackel and Gordy 1968). The signals from both $\cdot\text{PH}_2$ radical and $\cdot\text{P}$ atom are of comparable strength (figure 1). Therefore, the energy transfer mechanism dominating the photolysis is seen to be efficient enough to produce a sufficient number of radicals at isolated points in the cage structure, enabling subsequent investigation by EPR.

The electronic Zeeman level is first split by the ^{31}P nucleus (figure 1). This doublet, over 80 gauss wide, is further split by two H atoms (with a net spin of $\Sigma_i I_i = 1$ in the high field approximation), giving rise to a 6-line spectrum in which the intensity of the two triplets (spaced 23 gauss apart) is in conformity with the 1:2:1 pattern expected for the usual Boltzmann distribution of spin populations.

Further, a precise assessment of the spin Hamiltonian parameters of the $\cdot\text{PH}_2$ and $\cdot\text{P}$ atoms has been made through computer simulation of the entire composite lineshapes, assuming the following spin Hamiltonian

$$\mathcal{H}_s = g_0 \beta_e \mathbf{H} \cdot \mathbf{S} + A_0 \mathbf{I} \cdot \mathbf{S} \quad (1)$$

All calculations of the lineshapes have been carried out on a DEC 1090 computer using a program (Sur 1982) written on the basis of an elegant second-order perturbation procedure (Iwasaki 1974). It is assumed that the principal axes of all tensors are coincident. The simulated spectrum (dotted lines) shown in figure 2 is in satisfactory agreement with the experimental spectrum (solid lines). g -factors (g_0) and isotropic hyperfine splitting constants (A_0) used for the simulation, presented in table 1 show

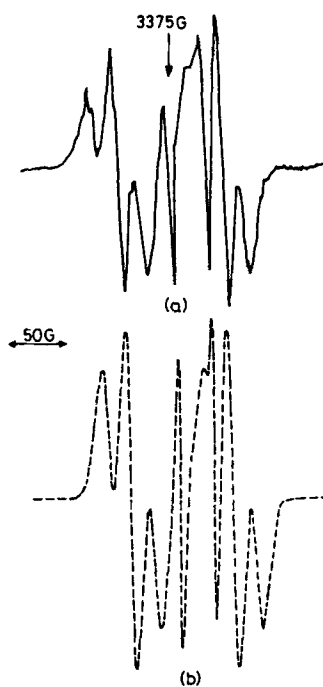


Figure 2. Computer simulation (b) of the experimental spectrum (a) shown in figure 1.

Table 1. g factors and hyperfine splitting constants for the photofragments of PH_3 .

Species	Matrix	Temperature (K)	g -factor	Isotropic hyperfine coupling constant ($\times 10^4 \text{ cm}^{-1}$ *)		Reference
				$A(^{31}\text{P})$	$A(^1\text{H})$	
$\cdot\text{PH}_2$	Krypton	4.2	2.0087	74.72	16.81	<i>a</i>
	Xenon	4.2	2.0050 ± 0.0010	76.39 ± 0.47	15.88 ± 0.93	<i>b</i>
	Cancrinite	77	2.0048 ± 0.0010	77.95 ± 0.5	21.56 ± 0.5	Present work
P atom	Free state	—	2.0019 ± 0.0004	—	—	<i>c</i>
	Free state	—	—	18.353 ± 0.0028	—	<i>d</i>
	Argon	4.2	2.0012 ± 0.0001	26.85 ± 0.09	—	<i>e</i>
	Krypton	4.2	2.0001 ± 0.0002	27.80 ± 0.56	—	<i>e</i>
	Xenon	4.2	2.0012 ± 0.0001	28.86 ± 0.93	—	<i>e</i>
	Cancrinite	77	1.9961 ± 0.0003	27.27 ± 0.19	—	Present work
**H atom	**Argon	4.2	2.00161 ± 0.00008	—	479.07 ± 0.33	<i>f</i>
	Argon	4.2	2.00108 ± 0.00011	—	479.11 ± 0.33	<i>e</i>
	Krypton	4.2	1.99967 ± 0.00031	—	476.02 ± 0.93	<i>f</i>
	Krypton	4.2	1.998941 ± 0.00014	—	476.69 ± 0.50	<i>e</i>
	Xenon	4.2	2.00057 ± 0.00008	—	468.85 ± 0.11	<i>f</i>
	Xenon	4.2	1.99999 ± 0.00008	—	469.08 ± 0.18	<i>e</i>
	Cancrinite	77	1.99875 ± 0.00010	—	470.27 ± 0.51	This work

* 1 Gauss = $0.0000934 \text{ cm}^{-1}$. ** g - and A -values are calculated using Breit-Rabi formula (Breit and Rabi 1931).

(a) Morehouse *et al* 1966 (b) Jackel and Gordy 1968 (c) Dehmelt 1955 (d) Pendlebury and Smith 1964 (e) Jackel *et al* 1968 (f) Foner *et al* 1960.

that the magnetic resonance parameters observed for PH_3 photofragments in cancrinite are compared with the results from earlier studies using rare gas matrices. The entries for g and A values in the last row of table 1 are for the H-atom, and these have been directly calculated from the experimental doublet using the well-known 'Breit-Rabi' equations (Breit and Rabi 1931).

The isotropic nature of the $\cdot\text{PH}_2$ spectrum leads to the inference that these radicals undergo rotational or tumbling motions at the sites of trapping within the cancrinite framework. The consequent population of the higher rotational levels naturally leads to the 1:2:1 intensity distribution (McCarty and Robinson 1959). In some of the earlier investigations performed at liquid helium temperature (Jackel and Gordy 1968), a 1:1:1 intensity pattern was observed for the $\cdot\text{PH}_2$ radical. This anomalous pattern was attributed either to a non-thermally-activated distribution of the nuclear spin states in the ground rotational state of the radical (McConnel 1958) or to partial microwave power saturation of the resonance lines.

4. Matrix effects

4.1 $\cdot\text{PH}_2$ radical

The matrix often plays an important role in altering the spin density distribution in the radical framework. In particular, in aluminosilicate matrices such as cancrinite, fairly

large electric fields are expected to be present (Kasai and Bishop 1976). The presence of such matrix fields is reflected by a shift in the hyperfine interaction of the trapped radical from that observed in other matrices (Vansant and Lunsford 1972) and in the 'free' state. Since the experimental data (table 1) clearly demonstrate shifts in the observed EPR parameters in going from one type of matrix to another, it would be interesting to estimate the bond-angle of $\cdot\text{PH}_2$ from the observed data in cancrinite. From the hyperfine splitting data, one can easily calculate the corresponding s -spin densities on the respective nuclei of $\cdot\text{PH}_2$ (Atkins and Symons 1967). $\rho_{\text{PH}_2}^{\text{P}}$, $\rho_{\text{PH}_2}^{\text{H}}$ and $\rho_{\text{P}}^{\text{P}}$ (table 2) denote, respectively, the isotropic experimental values of the $3s$ -spin density on ^{31}P of $\cdot\text{PH}_2$, the $1s$ -spin density on ^1H of $\cdot\text{PH}_2$, and the $3s$ -spin density on ^{31}P of isolated phosphorous atoms. The P atom, with its ground state configuration of $[\text{Ne}]3s^23p^3$, has the term symbol $^4\text{S}_{3/2}$. Therefore, in P atom, the isotropic spin density $\rho_{\text{P}}^{\text{P}}$ arises (Jackel *et al* 1968) mainly from 'core polarisation' of the inner s -orbitals by the unpaired electron. On the other hand, the spin density, $\rho_{\text{PH}_2}^{\text{P}}$, has contributions both from a 'core polarisation' term, which in this case may be equated to $\rho_{\text{P}}^{\text{P}}$, as well as from a term representing " σ - π " spin polarisation of the hybrid P-H bond. The data of table 2 shall now be analysed accordingly.

From its gas-phase rotational analysis (Dixon *et al* 1967), the ground state of the $\cdot\text{PH}_2$ radical has been established to be of C_{2v} symmetry. For the 7-electron system, the odd electron should then occupy a molecular orbital of b_1 symmetry consisting of a phosphorous p -orbital that is perpendicular to the molecular plane (say, in the x -axis). The species is thus a " π -radical". Open shell molecular orbital calculations performed at the CNDO/2 level, and the earlier report of Kilcast and Thompson (1972), predict unit spin density in the P_x orbital of phosphorous. In the light of these, the observed isotropic ^{31}P hyperfine interaction or the corresponding spin density, $\rho_{\text{PH}_2}^{\text{P}}$, is to be explained by invoking a spin polarisation mechanism, as mentioned earlier. As a consequence, there will be a negative spin density at the hydrogen nuclei of PH_2 . Now, the measured value of the latter quantity is represented as $\rho_{\text{PH}_2}^{\text{H}}$ in table 2. The corresponding positive spin density on the phosphorous bonding orbital will, of course, be twice this value, *i.e.*, 0.092. Taking this quantity to represent the spin polarization of the P-H bond by the unpaired P electron ($\rho_{\sigma\pi}^{\text{P}}$), one obtains for $\rho_{\text{PH}_2}^{\text{P}}$ the relation

$$\rho_{\text{PH}_2}^{\text{P}} = f_s(\rho_{\sigma\pi}^{\text{P}}) + \rho_{\text{P}}^{\text{P}}, \quad (2)$$

where f_s is the fractional s -character of the P-H bond.

Alternatively, the presence of p -orbitals on P suggests that the ' s -character' in the spin

Table 2. Spin densities derived from EPR data on PH_2 and P trapped in cancrinite.

Species	Nuclei	Hyperfine splitting $A_0 (\times 10^4 \text{ cm}^{-1})$	Spin density
$\cdot\text{PH}_2$	^{31}P	77.95	0.023 (= $\rho_{\text{PH}_2}^{\text{P}}$) ^a
	^1H	21.56	-0.046 (= $\rho_{\text{PH}_2}^{\text{H}}$) ^b
$\cdot\text{P}$	^{31}P	27.27	0.008 (= $\rho_{\text{P}}^{\text{P}}$) ^a

(a) The isotropic coupling of the 'free' P atom has been taken to be 3640 gauss (Atkins and Symons 1967). (b) The isotropic coupling of the H atom trapped in cancrinite (*i.e.* 503.5 gauss) has been used for ^1H spin density calculation.

density on P may also result from a 'configuration interaction' mechanism, wherein states involving unpaired *s*-spin at the nucleus are assumed to mix with a normal ground state where the unpaired electron may be mainly localised in the *p*-orbital. Any anisotropic components of the hyperfine tensor will, of course, be averaged out by fast tumbling motion of $\cdot\text{PH}_2$ such as is apparent in our experiment.

From equation (2), the fractional *s*-character of the P-H bond, f_s , is calculated to be 0.162. Using this value and assuming that the bonding orbitals are sp^2 hybrids with no *d*-orbital contribution, the H- $\hat{\text{P}}$ -H bond angle (θ) is calculated by making use of the following well-known relationship (Huhee 1978):

$$\theta = \cos^{-1} [f_s / (f_s - 1)]. \quad (3)$$

The above calculation leads to an angle of about 101° for $\cdot\text{PH}_2$ trapped in cancrinite. This value is compared with the bond-angle observed for $\cdot\text{PH}_2$ in the gas phase as well as angles reported from hyperfine interaction data obtained in rare gas matrices (table 3), where calculations have again been limited to *s* and *p* orbitals of phosphorous only.

It is seen from table 3 that, in cancrinite, there is a decrease in the H- $\hat{\text{P}}$ -H angle of only 2° - 3° from those observed in frozen rare gas matrices. It is also interesting that the *apparent* overall decrease in the angle from the gas phase value is as much as 9° . Although it is tempting to ascribe this discrepancy in the angle to a possible matrix interaction, it ought to be pointed out that calculations made with the explicit inclusion of even as little as 4% *d*-character in the $^2\text{B}_1$ ground state of $\cdot\text{PH}_2$ (Jordan 1964) has led to a substantial *reduction* of the H- $\hat{\text{P}}$ -H angle in the direction of the gas phase value.*

A further pertinent aspect is the *isotropic* nature of the ^{31}P and ^1H hyperfine couplings in PH_2 , which leads to the inference that the radical is trapped within pseudo-spherical cavities of cancrinite and fast tumbling motion averages out the anisotropies in the tensor components. Perturbational effects due to the matrix environment are therefore thought to be minimal for $\cdot\text{PH}_2$ in the cancrinite cage.

4.2 Phosphorous atom

The sharp doublet spectrum in the central region of figure 1, with a hyperfine line separation of 29.2 gauss (0.00273 cm^{-1}), is readily recognized to be due to the P atoms

Table 3. Structure of the PH_2 radical in various matrices.

Matrix	<i>s</i> character of P-H orbitals	Bond angle (degree)	Reference
Free state	—	91.7	Dixon <i>et al</i> (1967)
Krypton	0.19	104.0	Morehouse <i>et al</i> (1966)
Krypton	0.196	104.0	Calculated with the data of Jackel <i>et al</i> (1968)
Xenon	0.026	105.0	Jackel <i>et al</i> (1968)
Cancrinite	0.126	101.0	Present work

* The authors thank a referee for prompting this discussion.

isolated in the aluminosilicate matrix at 77 K. The general features of this spectrum agree well with those reported by Jackel *et al* (1968) in frozen rare gas matrices. Here again, the hyperfine coupling constant is close to that obtained in the Krypton matrix ($\sim 0.00278 \text{ cm}^{-1}$) suggesting roughly similar isotropic environment of P atoms in the two matrices. The g -value, however, is slightly lower than that observed in the Krypton matrix. The g - and A -values of P atom in cancrinite are also presented in table 1 where the 'free' state values are those obtained by direct atomic beam measurements on the P atoms in the vapour state (Dehmelt 1955; Pendlebury and Smith 1964). The observed shifts in the g and A values from the corresponding 'free' state values show a definite perturbation in the electronic state of the trapped P atoms. The magnitudes of these shifts are

$$\Delta g = -0.0057,$$

$$\Delta A = +9.55 \text{ Gauss } (= +0.000892 \text{ cm}^{-1}).$$

The matrix-induced g -shift indicates a contribution from the orbital angular momentum to the g -factor, thus lowering the g -value from that observed in the 'free' state. This may be accounted for at least qualitatively by considering the excitation of the P atom states by van der Waals interaction (Adrian 1962) with the matrix to states such as [Ne] $3s^1 3p^4$, giving rise to a term 4P and consequent orbital contribution to the g -factor.

Again, the nearly 50% increase in the hyperfine splitting constant from the 'free' state value of 19.65 gauss (0.00184 cm^{-1}) shows the operation of a mechanism such as 'configuration interaction' whereby s -spin density is increased on the P atoms isolated in cancrinite. In calculations involving configuration interaction, states such as [Ne] $3s^1 3p^3 4s^1$ are assumed to be mixed with the normal ground state configuration, the excited state being of the same symmetry as the normal ground state. The admixture of each state is, of course, determined by the minimisation of the overall energy criterion. Such calculations adequately identify the origin of the observed isotropic A -values for several group V atoms (Bessis *et al* 1961; Jackel *et al* 1968). However, this mechanism alone cannot explain our observed matrix shift of about 10 gauss in the A -value, and further consideration of an interaction between the trapped P atom and surrounding matrix atoms becomes necessary. Matrix effects would indeed be expected to be prominent in cancrinite at regions close to the charge-balancing cations (Smith 1976; Dempsey 1968). Calculations of electric field gradient in zeolitic structures (Dempsey 1968) have demonstrated that the electrostatic field could be several volts per angstrom at distances of 2.5 to 3 Å away from a multivalent cation, and such estimates have been experimentally substantiated in different zeolites (Smith 1976). Such a cationic field can perturb the electronic ground state of a sorbed paramagnetic species, thus resulting in a substantial shift in EPR hyperfine splitting constants (Coope *et al* 1971; Sugihara *et al* 1977) and g -tensor components (Lunsford 1968; Gardner and Weinberger 1970; Chao and Lunsford 1972; Kasai and Bishop 1972). Considering such sources of matrix interaction and the smaller size of the P atom (covalent radius = 1.1 Å), it is suggested that these atoms are trapped and stabilised in sites adjacent to a hexagonal window. Occluded salts and less porous cavities of the cancrinite framework effectively check the diffusion of these reactive species.

5. Conclusion

The zeolitic matrix of cancrinite effectively stabilises radicals such as $\cdot\text{PH}_2$, $\cdot\text{P}$ and $\cdot\text{H}$

with surprising facility. Computer simulation of the resultant composite EPR lineshapes from $\cdot\text{PH}_2$ and $\cdot\text{P}$ has been employed to assess the spin Hamiltonian parameters. The similarity of the EPR data of $\cdot\text{PH}_2$ trapped in cancrinite to that isolated in rare gas matrices, as well as the isotropic nature of the ^{31}P and ^1H hyperfine couplings in this work, lead to the inference that $\cdot\text{PH}_2$ is trapped in pseudo-spherical cavities with minimal matrix perturbations. Marked departures of the g - and A values of the trapped P atoms compared with reported gas-phase values are rationalised in terms of matrix induced interactions arising from factors such as the strong intrazeolitic cation fields present at the trapping site. Considering such sources of matrix interaction and the small size (covalent radius 1.1 Å) of the P atom, it is suggested that P is trapped and stabilised at a site adjacent to a hexagonal window of the zeolitic cage.

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