

GAMMA RADIOLYSIS OF 1,2-BIS(DIPHENYLPHOSPHINE)ETHANE IN METHANOL AND CYCLOHEXANE SOLUTIONS AND IN THE SOLID STATE

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Abstract - The decomposition yields of 1,2-bis(diphenylphosphine)ethane (dppe) in cyclohexane and in methanol solutions saturated with Ar or N₂O have been determined from the absorption decrease at 253 nm. The decomposition yields of dppe.HCl dissolved in Ar or N₂O saturated methanol have been determined, too. Taking into account the obtained results as well as the variations of the absorption bands and the HMR signals, a radiolysis mechanism has been suggested. Applying the steady state approximation, the reaction rate constants have been calculated: $k(e\bar{g} + dppe \cdot 2HCl) = 5.8 \cdot 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$; $k(H + dppe) = 2.89 \cdot 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$; $k(CH_3OH + dppe) = 1.16 \cdot 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$. Also the decomposition yield of dppe in the solid phase has been determined and ESR studies have been carried out.

INTRODUCTION

1,2-Bis(diphenylphosphine)ethane (dppe) belongs to the ligands employed frequently in order to stabilize the higher and the lowest oxidation states of transition metals¹⁻⁵. Compounds of transition metals with dppe are widely used for fixation and reduction of molecular nitrogen^{2,6-8}. The possibility of fixing and reducing molecular nitrogen by ultraviolet irradiation of Mo and W complexes with phosphines in a nitrogen atmosphere was reported.⁹ Ionizing radiation applied to the complex of Os(II) with N₂ (but without any other donor-acceptor ligands) in aqueous solution does not lead to the reduction of nitrogen.¹⁰

From the above facts we may conclude that the change of radiational fixing and reducing of N₂ depends notably on the stability of the ligand to stabilize the nitrogen complex. This ability results from the reactivity of the ligands towards unstable radiolysis products (beside their capacity to stabilize the low oxidation states of the central atom). This work was therefore aimed at the radical products as well as at getting some insight into the mechanism of the radiolysis of dppe. These studies will be extended later to radiational-chemical processes occurring in complexes of d-electron metals with dppe and N₂ under the influence of ionizing radiation.

RESULTS AND DISCUSSION

Typical changes in the absorption spectrum of dppe caused by irradiation are shown in Fig.1. As indicated in Fig.1, the irradiation results in an absorption decrease at 253 nm and in an appearance of a new band at about 230 nm. Because

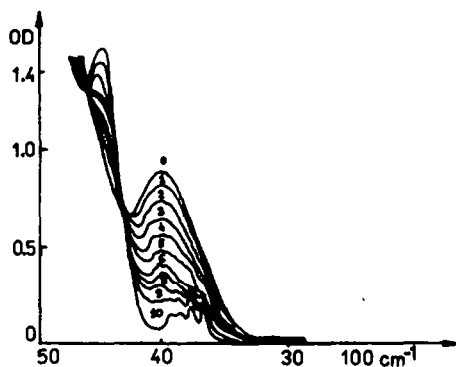


Fig.1. Variations in the absorption spectrum of dppe in methanol solution ($C = 10^{-4} \text{ mol dm}^{-3}$) irradiated with a dose : 0 - nonirradiated; 1 - $0.98 \cdot 10^{18}$; 2 - $1.96 \cdot 10^{18}$; 3 - $2.94 \cdot 10^{18}$; 4 - $3.92 \cdot 10^{18}$; 5 - $4.90 \cdot 10^{18}$; 6 - $5.80 \cdot 10^{18}$; 7 - $6.90 \cdot 10^{18}$; 8 - $7.80 \cdot 10^{18}$; 9 - $8.80 \cdot 10^{18}$; 10 - $9.80 \cdot 10^{18} \text{ eV ml}^{-1}$.

of the position and high intensity, the 253 nm band may be attributed to the charge-transfer transition of π electrons of the phosphorus d orbitals. Indirect evidence of this delocalisation is different frequency of valence vibrations of $\text{P-C}_{\text{aromatic}}$ (1440 cm^{-1})¹¹ in comparison with $\text{P-C}_{\text{aliph.}}$ ($1280 - 1320 \text{ cm}^{-1}$)¹¹. The alternative $\pi \rightarrow \pi^*$ transition, acceptable because of its position (230 - 260 nm) would have a much lower intensity since it is forbidden because of symmetry.¹² The intensity decrease at 253 nm caused by irradiation is related to the disruption of C-P bond. C_6H_6 , formed in this effects, shows a vibrational structure of the band of low intensity attributed to the $\pi \rightarrow \pi^*$ transition (see Fig.1).

The 230 nm band, taking into account its position and intensity, may be attributed to the charge-transfer transition of the $-\text{CH}=\text{CH}-$ π electrons to the d orbitals of phosphorus. The double bond of the $-\text{CH}=\text{CH}-$ group results from the removal of hydrogen from $-\text{CH}_2-\text{CH}_2-$. The phosphine with ethylene group $\left(\begin{array}{c} \text{Ph} \\ | \\ \text{P}-\text{CH}=\text{CH}-\text{P} \\ | \quad | \\ \text{Ph} \quad \text{Ph} \end{array} \right)$ is well known.¹³

The above interpretation of the variations in absorption shown in Fig.1 are confirmed by the results of NMR studies of both the non-irradiated and irradiated dppe : ¹HMR signals at 2.1 ppm (triplet) resulting from $-\text{CH}_2-\text{CH}_2-$ as well as the signal at 7.45 ppm resulting from C_6H_5 group both decrease, while at 7.65 ppm and 7.1 ppm there appear new distinct signals related to the C_6H_6 and $-\text{CH}=\text{CH}-$ groups respectively.

The number of decomposed molecules of dppe and $\text{dppe} \cdot 2\text{HCl}$ in methanol and of dppe in C_6H_{12} saturated with argon or N_2O depend non-linearly on dose and concentration as illustrated in Fig.2. The radiation decomposition yields of dppe and $\text{dppe} \cdot 2\text{HCl}$ are shown in Table I.

From inspection of Table I, one learns that in argon saturated solutions the decomposition yield is higher only in the case of $\text{dppe} \cdot 2\text{HCl}$. It may therefore be concluded that $\text{dppe} \cdot 2\text{HCl}$ is decomposed by e_s^- . In methanol solutions, dppe reacts with the $\cdot\text{CH}_2\text{OH}$ radicals as indicated by a little higher yield in the presence of N_2O . In cyclohexane, the decomposition yield does not depend on the saturating gas practically. Consequently, in cyclohexane dppe reacts with H atoms.

In the solid phase, the number of decomposed dppe molecules is a linear function of the dose in the investigated dose range. The decomposition yield of

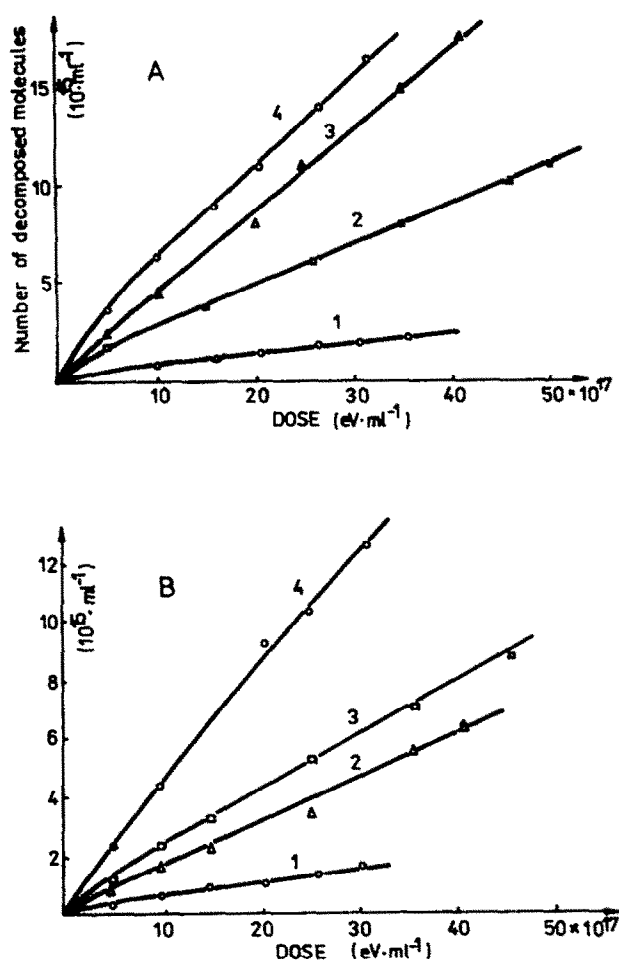


Fig.2. The number of decomposed dppe·2HCl molecules in methanol solutions saturated with argon (A) and with H_2O (B) as functions of the dose and concentrations : 1 - $1 \cdot 10^{-4}$; 2 - $3 \cdot 10^{-4}$; 3 - $5 \cdot 10^{-4}$; 4 - $7 \cdot 10^{-4}$ mol dm^{-3} .

Table I. Decomposition yields of dppe and dppe·2HCl in solutions

Methanol solutions							Cyclohexane solutions		
C mol dm^{-3}	dppe·2HCl		ΔG_1^*	dppe		ΔG_2^*	C mol dm^{-3}	satur. with Ar	satur. with N_2O
	satur. with Ar	satur. with H_2O		satur. with Ar	satur. with H_2O				
$1 \cdot 10^{-4}$	0.16	0.08	0.08	0.114	0.12	0.006	$1 \cdot 10^{-4}$	0.07	0.09
$3 \cdot 10^{-4}$	0.35	0.17	0.18	0.160	0.23	0.070	$5 \cdot 10^{-4}$	0.23	0.24
$5 \cdot 10^{-4}$	0.52	0.23	0.29	0.200	0.31	0.110	$1 \cdot 10^{-3}$	0.46	0.54
$7 \cdot 10^{-4}$	0.76	0.43	0.33	0.300	0.45	0.150	$5 \cdot 10^{-3}$	1.50	1.60

$\Delta G_1^* = G(-dppeH_2^{2+})$ solution saturated with Ar - $G(-dppeH_2^{2+})$ solution saturated with H_2O

$\Delta G_2^* = G(-dppe)$ solution saturated with H_2O - $G(-dppe)$ solution saturated with Ar

dppe in the solid phase equals 1.69 molecules per 100 eV.

The ESR signals of irradiated dppe in solid phase is shown in Fig.3. Fig.3

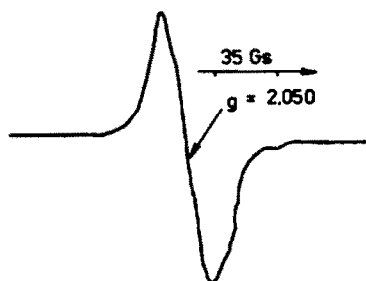


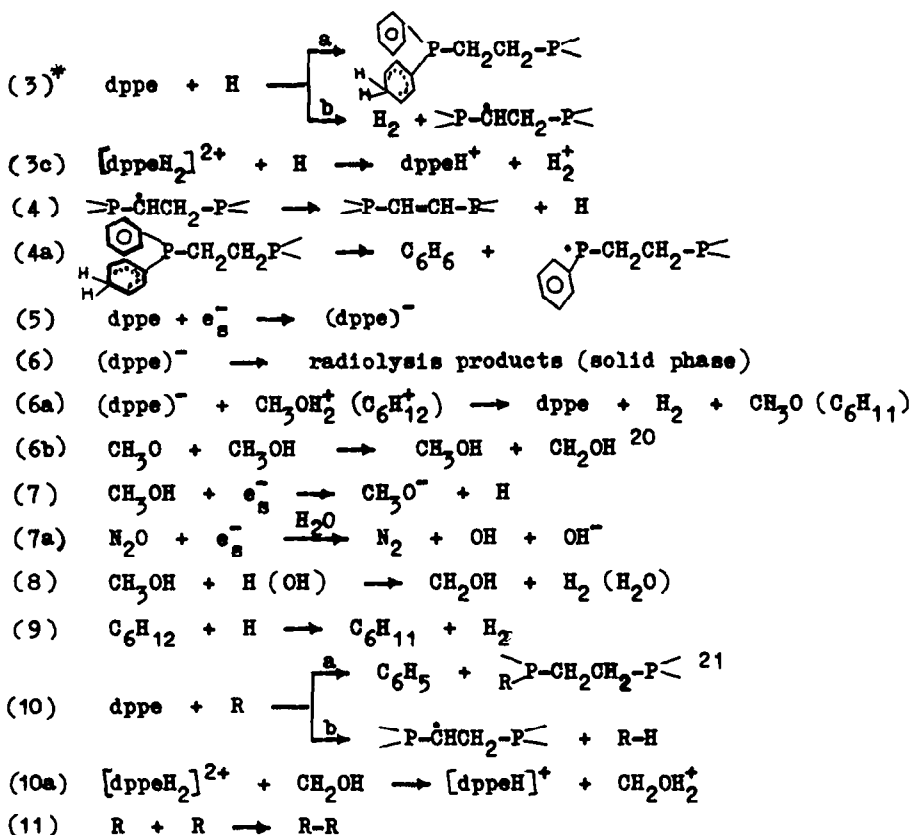
Fig.3. ESR signal at 130 K of dppe irradiated in the solid phase by a dose 10 kGy.

indicates that the irradiation of dppe results in a non-resolved signal of $g_{av} = 2.059$. This signal is vanishing at 210 K and its shape remaining unchanged. Keeping in our minds an axial symmetry of the paramagnetic centre ($g_{av} = 2.059$) and band width we can relate this ESR signal to the anion-radical $(dppe)^-$. Formation of similar anion-radicals by the addition of e^- to the phosphines were observed by some of authors.¹⁴⁻¹⁷ According to analysis of the superfine structure of the spectra and on the value of the g parameter ($g_{av} = 2.0023$; $\Delta g = 0.001$) it is assumed that for the anion radicals $(Ph_3P)^-$ or $(Ph_3P=O)^-$ the unpaired electrons were delocalized in the entire aromatic rings (π^*).¹⁵⁻¹⁶ On the other hand calculations of the electronic charge distribution in $(Ph_3P=O)^-$ based on Hückel method, gave the following density values of the unpaired electron at the C_2-H , C_4-H and P atoms: $\int_P = 0.21$, $\int_{H-C_2} = 0.083$ and $\int_{H-C_4} = 0.084$, respectively.¹⁵ A good agreement between the experimental and the calculated values was found: $\int_{H-C_2} = \int_{H-C_4} = 0.076$.¹⁵ Taking into account the g -parameter anisotropy it is assumed that the \int_P -parameter in $(dppe)^-$ is higher than in $(Ph_3P=O)^-$ and the unpaired electron is located on 3d orbital. Due to anisotropy we can find the doublet ($a^P = 0.87$ mT) with non-equivalent intensity in the ESR spectrum (Fig.3). Above mentioned a^P value is in good agreement with the literature data.¹⁵ The approximate value of the \int_P -parameter ($\int_P = 0.368$) was determined from the a^P value as well as from the Mc Connel relation for $\int < 1$ ¹⁸ and assuming that Q_{C-P}^P is equal Q_{C-H}^H (theoretical value for Q_{C-H}^H is ca. 2.36 mT).¹⁹

The lower yield of decomposition of dppe in solutions saturated with argon does not rule out the possibility of formation of $dppe^-$ anions. The disappearance of $dppe^-$ may occur in a reaction with $C_6H_{12}^+$ or $CH_3OH_2^+$ without the decomposition of dppe. This conclusion seems to be confirmed by the higher decomposition yield in the solid phase.

Taking into consideration the above results, the following mechanism of the radiolysis of dppe may be assumed:

- (0) $S \xrightarrow{\gamma} e_s^-, S^+, H, R$
- (1) $[dppeH_2]^{2+} + e_s^- \rightarrow [dppeH_2]^+$
- (2) $[dppeH_2]^+ \begin{cases} \xrightarrow{a} \text{radiolysis products} \\ \xrightarrow{b} dppe + H_2^+ \end{cases}$



* - The formation of alkyl radicals by thermal hydrogen atoms has been well known for a long time²² and the addition of hydrogen atoms to aromatic rings has been observed many authors²³⁻²⁶.

The employment of the steady state approximation to reactions 1 and 7 lead to the relationship I, while the same approximation applied to reactions 5 and 9 and to reactions 10 and 11 leads to II and III, respectively :

$$\begin{aligned}
 \text{I} \quad \frac{1}{\Delta G_1} &= \frac{1}{G_{e_{\text{e}}^-}} + \frac{k_7 [\text{CH}_3\text{OH}]}{k_1 [\text{dppeH}_2^{2+}] G_{e_{\text{e}}^-}} \\
 \text{II} \quad \frac{1}{G(-\text{dppe})} &= \frac{1}{G_{\text{H}}} + \frac{k_9 [\text{C}_6\text{H}_{12}]}{k_3 [\text{dppe}] G_{\text{H}}} \\
 \text{III} \quad \frac{1}{\Delta G_2} &= \frac{1}{G_{\text{CH}_2\text{OH}}} + \sqrt{\frac{2k_{11}}{G_{\text{CH}_2\text{OH}}}} \cdot \frac{1}{k_{10} [\text{dppe}]}
 \end{aligned}$$

ΔG_1 and ΔG_2 - see on the table

The dependence of $1/\Delta G$ and $1/G$ on $1/G$ are shown in Figs. 4 and 5, respectively. From Fig. 4 (line 1) the values of $G_{e_{\text{e}}^-} = 0.59$ and $\frac{k_7 [\text{CH}_3\text{OH}]}{k_1 G_{e_{\text{e}}^-}} = 1.07 \cdot 10^{-3}$ were

determined. From those values results $k_7/k_1 = 2.59 \cdot 10^{-5}$. Assuming $k_7 = 1.5 \cdot 10^4$ $\text{l mol}^{-1} \text{s}^{-1}$ ²⁷, the value of k_1 was found equal $5.8 \cdot 10^8$ $\text{l mol}^{-1} \text{s}^{-1}$. It results $G_{\text{CH}_2\text{OH}} = 1.0$ and $\sqrt{\frac{2k_{11}}{G_{\text{CH}_2\text{OH}}}} \cdot \frac{1}{k_{10}} = 4.23 \cdot 10^{-3}$ from the line 2 in Fig. 4.

Assuming $2k_{11} = 4.3 \cdot 10^9$ $\text{l mol}^{-1} \text{s}^{-1}$ ²⁷, $k_{10} = 1.16 \cdot 10^7$ $\text{l mol}^{-1} \text{s}^{-1}$.

From Fig. 5 $G_{\text{H}} = 1.1$ and $\frac{k_9 [\text{C}_6\text{H}_{12}]}{k_3 G_{\text{H}}} = 1.59$ and consequently $k_9/k_3 = 1.7 \cdot 10^{-4}$.

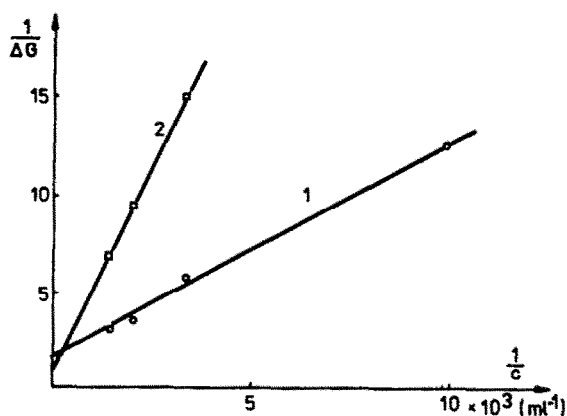


Fig. 4. Dependence of $1/\Delta G$ on the reciprocal concentration of $\text{dppe} \cdot 2\text{HCl}$ (line 1) and dppe (line 2) in methanol.

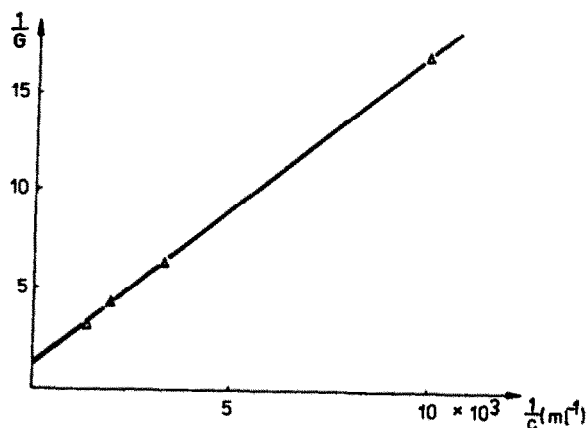


Fig. 5. Dependence of $1/G$ on the reciprocal concentration of dppe in cyclohexane saturated with argon.

Assuming $k_9 = 4.9 \cdot 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ ²⁷, the value of k_3 was found equal to $2.89 \cdot 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$.

From the above results one may conclude that dppe shows high reactivity towards H atoms and a moderate reactivity towards OH_2OH . The decomposition by solvated electrons is limited to protonated dppe .

From the results of these studies, we are led to conclude that dppe as ligand does not react with the electrons. The irradiation of the complex of Mo(IV) with dppe indicated that the ligand remains unchanged. ^{28,29}

EXPERIMENTAL

dppe (Fluka) was purified by a repeated extraction with petroleum ether and crystallisation from methanol. For the purified dppe $\epsilon_{253\text{nm}} = 1.65 \cdot 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, was found in cyclohexane.

$\text{dppe} \cdot 2\text{HCl}$ was obtained by dissolving dppe in a 2 M solution of HCl at lowered temperature (about 220 K).

Methanol and cyclohexane of analytical grade were used without further purification.

The solutions of dppe in methanol or cyclohexane were saturated with argon or H_2O for 15 minutes and after that irradiated with a dose rate of $1.63 \cdot 10^{16}$ eV $\text{cm}^{-3} \text{s}^{-1}$, using a cobalt source (Issliedovatiei, USSR). After irradiation, the solutions were diluted with the appropriate solvent to the concentration of $5 \cdot 10^{-5}$ mol dm^{-3} and their absorption was measured at 253 nm.

The dose was measured with Fricke's dosimeter and corrected for electron density of methanol and cyclohexane.

Samples of solid dppe put in glass tubes which were filled with argon after deaeration and sealed. Afterwards, the sealed tubes were irradiated.

The ESR spectra were recorded with JEOLCO JES-ME-3X spectrometer by using non-signal spectroil capillaries. NMR signals were measured with BS-487C spectrometer. For the spectrophotometric measurements Beckman 5240 and Specord UV-VIS spectrophotometers were used.

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