

TRIPLET STATE OF 1,10-PHENANTHROLINE AND BENZOPHENONE  
IN BENZENE STUDIED BY PULSE RADIOLYSIS

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From comparison of pulse radiolysis and laser photolysis of benzene solution of 1,10-phenanthroline /P/ and from the effect of N<sub>2</sub>O, O<sub>2</sub> and benzophenone it can be deduced that in radiolysis of benzene solution of P the triplet state P<sup>T</sup> is formed. It is characterized by a broad absorption band with two peaks at 420 and 440 nm. It decays according to first order kinetics with rate constant  $(3.1 \pm 0.5) \times 10^5 \text{ s}^{-1}$  yielding, at least partly, a product with absorption in UV. The rate constant for energy transfer from benzophenone triplet to P is  $(2.1 \pm 0.9) \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

## INTRODUCTION

In our previous work<sup>1,2</sup> we studied characteristic intermediates formed in the radiolysis of 1,10-phenanthroline /P/ aqueous solutions. As the typical intermediate products OH, H and e<sub>aq</sub><sup>-</sup> adducts were found with

characteristic absorption bands, yields, pK values and kinetical properties. Quite different situation can be expected in nonpolar solvents. This study is devoted to benzene as a solvent with low G /free ion/ and significant yields of excited states<sup>3</sup> which enables us to study the possible formation of excited states of P.

## EXPERIMENTAL

### Materials

1,10-phēnanthroline monohydrate /Lachema, p.a. grade/ was used as received. The anhydrous form was prepared from the monohydrate in vacuum under  $P_2O_5$  at elevated temperature; the powder was then recrystallized from purified benzene and dried again in vacuum under  $P_2O_5$ ; its melting point was 117 to 118 °C. Benzophenone /pure/ was triply recrystallized from ethyl ether. Benzene /Lachema, p.a. grade/ was three times treated with conc. sulphuric acid, repeatedly washed with water, dried with potassium hydroxide, anhydrous calcium chloride and finally with sodium wire and then fractionated; before use benzene was passed through a column filled with neutral  $Al_2O_3$ . The solutions were saturated by bubbling with Ar,  $O_2$  /both purest grade/ or  $N_2O$  /for medical use/.

### Pulse radiolysis and laser photolysis

Pulse radiolytic equipment in the Institute of Nuclear Research in Řež<sup>4</sup> with electron energy 4 MeV, pulse length 2.5  $\mu s$  and dose per pulse about 100 Gy or equipment in the Central Institute of Isotope and Radiation Research in Leipzig<sup>5</sup> with electron energy 1.0 MeV and pulse length 8 ns and dose per pulse about 50 Gy were used. The laser photolysis was performed in Leipzig with  $N_2$ -laser at

337 nm and with 1.8 ns pulse length using the same detection system as for the pulse radiolysis.

### Dosimetry

The dose per pulse was determined using oxygen saturated  $0.005 \text{ mol dm}^{-3}$  aqueous  $\text{K}_4\text{Fe}(\text{CN})_6$  taking  $G_{\text{e}/\text{Fe}(\text{CN})_6^{3-}/420} = 320 \text{ ion} / 100 \text{ eV} / \text{m}^2 \text{ mol}^{-1}$ . A simple density factor was used to calculate doses given to benzene solutions.

### Calculations

Numerical analysis of kinetic data was performed on the EC 1040 computer /Robotron, GDR/ or on the mini-computer ADT 4100 /ZVP Turnov, ČSSR/.

## RESULTS

The optical absorption spectrum of the intermediate formed by the pulse of ionizing radiation in benzene solution of P monohydrate saturated with Ar has the maximum with two peaks at 420 and 440 nm /see Fig. 1./ . The width of the band is significantly greater than that corresponding to benzophenone intermediate /see Fig. 1./ . By saturation of the solution with  $\text{N}_2\text{O}$  the absorption is slightly reduced; at the concentration  $0.02 \text{ mol dm}^{-3}$  - P the decrease of absorption amounts to about 14%. Saturation with  $\text{O}_2$  eliminates the absorption almost completely. Radiolysis of P anhydrous solution gives practically identical results. Nearly similar spectrum is obtained also with  $\text{N}_2$ -laser photolysis /compare the curves in Fig. 1./ .

Similar experiments were carried out with benzophenone /BP/. It is known that radiolysis of BP in benzene solutions leads to the formation of the triplet state

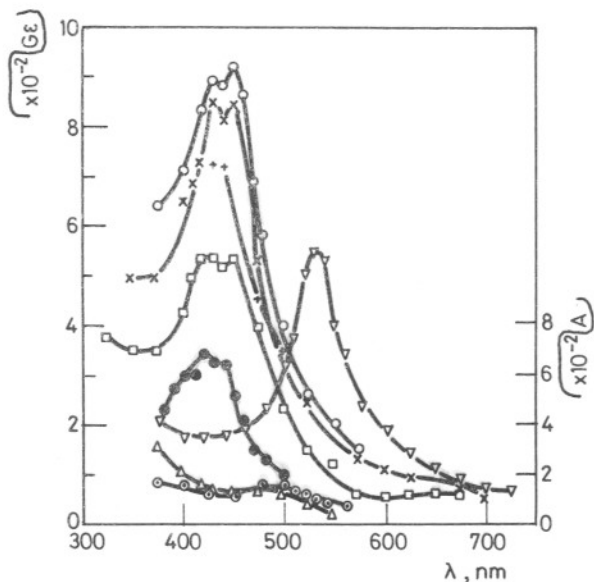


Fig. 1. The absorption spectra observed at the end of 2.5  $\mu\text{s}$  electron pulses and 1.8 ns laser pulses in benzene solutions of 1,10-phenanthroline and benzophenone. 0.02 mol  $\text{dm}^{-3}$  P. anhydrous saturated with Ar / $\circ$ /, 0.02 mol  $\text{dm}^{-3}$  P monohydrate with Ar /x/, with  $\text{N}_2\text{O}$  /+/,  $\text{O}_2$  / $\Delta$ /; 0.004 mol  $\text{dm}^{-3}$  P monohydrate with Ar / $\square$ /; 0.001 mol  $\text{dm}^{-3}$  BP with Ar / $\nabla$ /, with  $\text{O}_2$  / $\bullet$ /; all for electron pulses and related to the left ordinate; 0.02 mol  $\text{dm}^{-3}$  P monohydrate with Ar / $\bullet$ /, laser pulses, related to the right ordinate;  $G\epsilon$  in molec. /100 eV $^{-1}$  m $^2$ mol $^{-1}$  units

BP<sup>T</sup> with absorption maximum at 533 nm /see for example<sup>6</sup>/. Absorption spectra obtained in this work are given also in Fig. 1. Saturation with  $\text{N}_2\text{O}$  leads to a decrease of about 57%, as it was already observed<sup>7</sup> and of about 91% with  $\text{O}_2$ .

After the decay of the intermediate species in the P solutions a stable absorption at 430 nm and at shorter wavelengths remains belonging evidently to a stable product. This observation was verified by measuring the absorption long times /10<sup>0</sup> to 10<sup>1</sup> min/ after irradiation

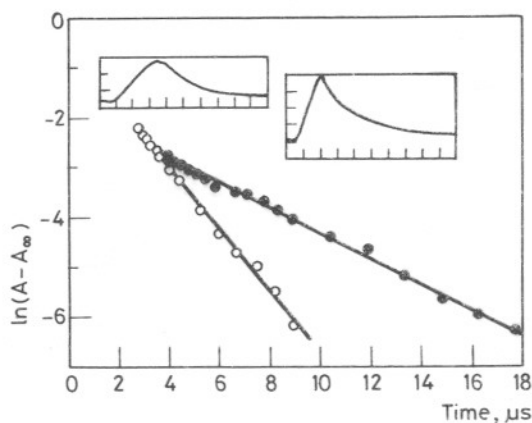


Fig. 2. The decay kinetics of the absorption at 430 nm<sup>-2</sup> and 530 nm in benzene solutions of 0.002 mol dm<sup>-3</sup> P (●) and 0.04 mol dm<sup>-3</sup> BP (○) saturated with Ar after the 2.5 μs electron pulse. A - absorbance in time t, A<sub>∞</sub> - stable absorbance 0.010 and 0.006 for P and BP, respectively, when the decay is finished; in the insets are the CRT traces, right for P with 2 μs and absorbance 0.05 per division, left for P with 1 μs and absorbance 0.1 per division; dose per pulse 90 Gy

by conventional spectrophotometry. The stable absorption was found to begin at about 470 nm and passes over a shoulder peak at 383 nm to high values below 350 nm. The G<sub>ε</sub> values in 0.007 mol dm<sup>-3</sup> P at 430 and 383 nm are about 27 and 61 molec. /100 eV<sup>-1</sup> m<sup>2</sup> mol<sup>-1</sup>, respectively.

The decay of absorption at 430 nm /the middle of the absorption band/ was analyzed taking into account the formation of the stable absorption in the concentration range of P from 0.004 to 0.04 mol dm<sup>-3</sup>. The first order kinetics fits the experiments /see Fig. 2./ and the rate constant is independent of P concentration. Its mean value is  $(3.1 \pm 0.5) \times 10^5 \text{ s}^{-1}$ . In solutions saturated with N<sub>2</sub>O and in solutions of P anhydrous saturated with Ar values  $2.7 \times 10^5$  and  $2.6 \times 10^5 \text{ s}^{-1}$  were obtained, resp.

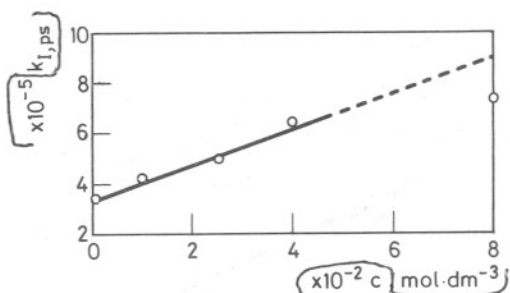


Fig. 3. Dependence of the pseudofirst order rate constant for the decay of the triplet state  $\text{BP}^{\text{T}}$  on the concentration of BP. 2.5  $\mu\text{s}$  electron pulses /x/, 1.8 ns laser pulses /o/

Comparable results were obtained also in the laser photolysis.

Kinetics of the decay of  $\text{BP}^{\text{T}}$  corresponds also to a first order process /see Fig. 2./. The rate constant varies as ~~does~~ BP concentration /see Fig. 3./, may be also due to impurities in BP according to

$$k_{I,ps} = k_I + k_{II}^{\text{C}} \text{BP} \quad /1/$$

where  $k_{I,ps}$  is the pseudo-unimolecular rate constant and hence  $k_I = 3.3 \times 10^5 \text{ s}^{-1}$ .

The absorption spectrum of pulse irradiated solutions of P and BP is a composite one with absorption bands corresponding to both components. The  $G_{\epsilon}$  values at 430 nm increase with P concentration and the  $G_{\epsilon}$  values at 530 nm decrease accordingly.

The time profiles of absorption were measured at 430 and 530 nm in the solution of BP and P irradiated with 8 ns pulses. These measurements were carried out at BP concentration 0.1 and P concentration 0.0002, 0.0005 and 0.001  $\text{mol dm}^{-3}$ . For kinetic analysis the experimentally found absorbancies  $A_{430,exp}$  and  $A_{530,exp}$  were cor-

rected for contribution of absorption of the other component<sup>x</sup>.

For the energy transfer the reaction



was anticipated where the transfer rate constant  $k_{tr}$  is given by the obvious relation

$$\ln \frac{G_{\epsilon_{as}}}{G_{\epsilon} - G_{\epsilon_{as}}} = k_{tr} c_P t \quad /3/$$

$G_{\epsilon_{as}}$  is the asymptotic value of  $G_{\epsilon}$  of  $P^T$  at long times. Curves obtained in this way are presented in Fig. 4. The mean value of  $k_{tr}$  is  $2.1 \pm 0.9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . This value is identical with the value of the rate constant found for simultaneous decay of  $BP^T$  according to reaction /2/ observed at 530 nm. Value of  $k_{tr}$  found is about 40% of the diffusion controlled rate constant.

<sup>x</sup>Following approximations were used:

$$A_{P,430} = \frac{A_{430,exp} - A_{530,exp} p_{BP}}{1 - p_P p_{BP}},$$

$$A_{BP,530} = A_{530,exp} - \frac{A_{430,exp} - A_{530,exp} p_P}{1 - p_P p_{BP}},$$

where  $p_P = A_{530}/A_{430}/P$  and  $p_{BP} = A_{430}/A_{530}/BP$  in solution of P or BP /see Fig. 1./.

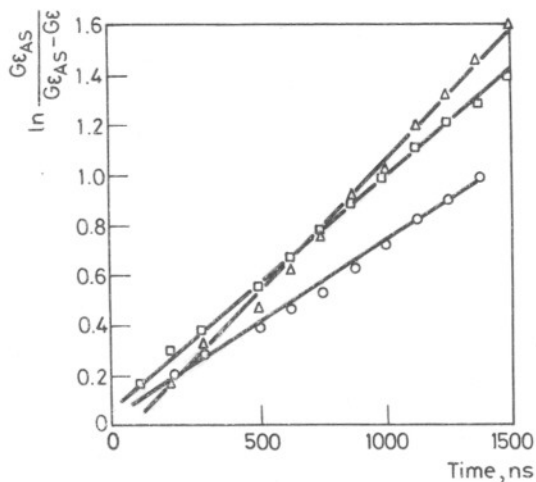


Fig. 4. The kinetics of the  $P^T$  formation via energy transfer from  $BP^T$  to P according to the relation  $\ln \frac{G_{eAS}}{G_{eAS} - G_e}$  in the text. Benzene solutions of  $0.01 \text{ mol dm}^{-3}$  BP and  $0.0002$  /O/,  $0.0005$  /□/,  $0.001 \text{ mol dm}^{-3}$  P /Δ/, all Ar saturated and with 8 ns electron pulses

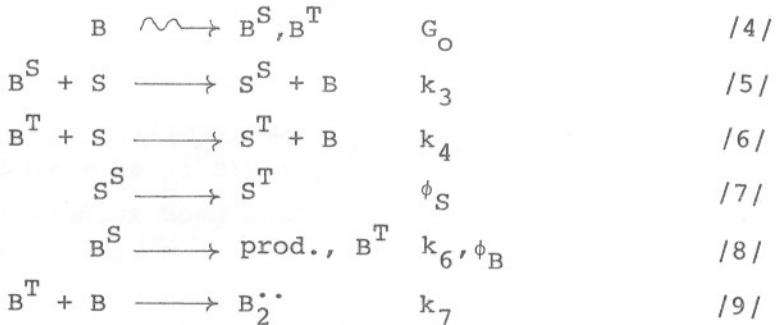
## DISCUSSION

Identical results obtained in pulse radiolysis and laser photolysis, effect of  $N_2O$  and  $O_2$  on the yield of intermediate and observed energy-transfer reaction between  $BP^T$  and P confirm the conclusion that the absorption found in benzene solution of P at 430 nm belongs to a triplet state of P. The effect of  $N_2O$  shows that the contribution of electron-cation recombination to formation of  $P^T$  is small. The width of the  $P^T$  absorption band is significantly greater than that of  $BP^T$  and has two peaks with an energy difference of about 0.13 eV. The two peaks may correspond to the  $^3/n, \pi^*$  and  $^3/\pi, \pi^*$  states, considered already in the photolysis of P in cyclohexane where peaks at 442 and



422 were found<sup>8</sup>. Similar two peaks were observed also in PMMA matrix with P at 77 K /see Ref. 9/. Water originally present in the used P monohydrate is not involved in the triplet state since with anhydrous form of P the same results were obtained.

For the mechanism of  $BP^T$  and  $P^T$  formation we use the analogous reaction scheme as outlined by Baxendale and Fiti<sup>10</sup> or Gangwer and Thomas<sup>11</sup>



where B is benzene, S is BP or P,  $G_O$  are the primary yields of singlet and triplet states of benzene,  $B^S$  represents both monomer and excimer singlet state of benzene which are believed to be in a rapid equilibrium<sup>10</sup>, and  $\phi_S, \phi_B$  are the efficiency coefficients of the ISC. For total yield of triplet state of the solute in question we can derive a relation

$$\begin{aligned}
 G/S^T/_{\text{tot}} = \{ G/B^T/O + G/B^S/O & \left[ \phi_S \frac{k_3/k_4 c_S + k_7/}{k_4/k_3 c_S + k_6/} + \right. \\
 & \left. + \phi_B \frac{k_6}{k_6 + k_3 c_S/} \right] \} \frac{k_4 c_S}{k_4 c_S + k_7/}, & /10/
 \end{aligned}$$

which in the reciprocal form reads as

$$\frac{1}{G/S^T/_{tot}} = \frac{1}{\{G/B^T/O + G/B^S/O\} F} / 1 + \frac{k_7}{k_4 c_S} /, \quad /11/$$

where F denotes the expression in square brackets in the relation /10/. F is a function of the solute concentration and the slope of the plot of  $1/G/S^T/_{tot}$  versus  $1/c_S$  cannot be constant. For high enough S concentrations F tends to a limiting value equal to  $\phi_S$ . From the sections on the ordinate obtained by extrapolating the curves, i.e.  $2.6 \times 10^{-4}$  for BP and  $5.6 \times 10^{-4}$  for P, using the  $BP^T$  extinction coefficient  $763 \text{ m}^2 \text{ mol}^{-1}$  /see Ref. 6/, we get  $G/B^T/O + G/B^S/O \phi_S = 5.04$ . For  $\phi_S$  in the case of BP equal to 1 used in Ref. 11, we get for the sum of the yields of excited singlet and triplet species formed in benzene radiolysis a value about 5.0 which is by about 15% smaller than the value presented as the most probable one /for a review see 3/.

The products of the decay of both  $BP^T$  and  $P^T$  were not analyzed but the final stable absorption in both cases shows that  $BP^T$  and  $P^T$  are converted at least partly in chemically new species. The most probable interpretation of the first order decay of  $P^T$  is a reaction with benzene with the corresponding bimolecular rate constant  $k_{/P^T+B/} = 2.7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Similarly  $BP^T$  may decay in a reaction with benzene with a rate constant  $k_{/BP^T+B/} = 2.9 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Further  $BP^T$  may react also either with BP in the ground state or more probably with some reactive impurity in BP what is indicated by the second term in relation /1/. One cannot of course exclude a simultaneous simple radiationless transition from the triplet state to the singlet ground state without chemical change both in the case of  $BP^T$  and  $P^T$ .

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