Reaction of the phosphate radical with amines — A flash photolysis study

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Abstract. Rate constants for the reaction of phosphate radical with some aromatic and aliphatic amines have been determined by the flash photolysis technique. The products formed under conditions of continuous irradiation have been identified. In the case of an aromatic amine the major product is the azo compound while in the case of an aliphatic amine a carbonyl compound is formed.

Keywords. Flash photolysis; phosphate radical; rate constants; aromatic and aliphatic amines.

1. Introduction

In recent years considerable amount of attention has been paid to studies relating to the generation and reactions of inorganic radicals (Ross and Neta 1979; Morkovnik and Okhlobystein 1979). Most of these radicals are oxidising in nature and are postulated as intermediates in many thermal reactions. However, the intermediates or stable products in such reactions have been identified only in a limited number of cases and a systematic study in this respect is lacking. In thermal reactions, though radical generation and radical reaction steps have been postulated, the corresponding rate constants have not been evaluated. In this paper, we report the results of a study on the oxidation of amines with the phosphate radical.

The phosphate radical is a good oxidising agent and in general, two types of reactions take place, viz, hydrogen abstraction and electron transfer (Maruthamuthu and Neta 1977b; Maruthamuthu and Neta 1978). The acid-base forms and the corresponding optical absorption properties of phosphate radical are summarized in table 1 (Maruthamuthu and Neta 1978).

Table 1. Acid base forms and optical absorption properties of phosphate radical.

	$H_2PO_4^{\cdot}$	$HPO_4^{-\cdot}$	$PO_4^{2-\cdot}$
pK_a	5·7	8·9	
λ_{max}	520	510	530 nm
ε_{max}	1850	1550	2150 M^{-1} cm^{-1}

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2. Experimental

2.1 *Materials*

Only analytical grade chemicals were used in this investigation. Lithium peroxy-diphosphate ($Li_4P_2O_8 \cdot 4H_2O$) was prepared and purified as reported in the literature (Creaser and Edwards 1972; Maruthamuthu 1974; Maruthamuthu and Neta 1977a). Freshly distilled samples of amines were used for preparing the solutions. In the case of some solid amines, recrystallised samples were used and their purity checked from their melting points.

2.2 *Measurements*

Flash photolysis experiments were carried out in a Nortech Flash Photolysis apparatus described previously (Elango *et al* 1984). The half width of the flash duration was about 30 microseconds. The decay of the phosphate radical was monitored by following the absorbance at 530 nm and measurements were made at $23 \cdot 0 \pm 1 \cdot 0°C$. Continuous photolysis experiments were carried out with 48 W low pressure Hg lamps (Rayonet RUL 2537 Å). All solutions were prepared with triply distilled water and deaerated with purified nitrogen before flashing. The flash experiments were done within 20 min after mixing the solutions and used only for a single flash.

2.3 *Product analysis*

Continuous irradiation experiments were carried out to identify the end products. In a typical experiment, a well-cooled deaerated aqueous solution containing 5 mM peroxydiphosphate and 1 mM amine at pH $11 \cdot 0$ (NaOH was used to adjust the pH) was irradiated in a quartz tube with 254 nm radiation for about 30 min. Immediately after irradiation, the organic materials were extracted into ether from the alkaline medium. The ether extract after drying over anhydrous $MgSO_4$ was evaporated to a small volume and analysed.

The reaction products were carbonyl compounds in the case of aliphatic amines, as determined by GLC. These have also been identified by comparing the IR spectra of the phenylhydrazones of these compounds with those of authentic samples.

In the case of aniline, the products were analysed by TLC. 4-Aminodiphenyl-amine, azobenzene and benzidine are the major products, and 2-aminodiphenyl-amine and hydrazobenzene are formed in trace amounts. In addition, phenyl-hydroxylamine is also formed. Azobenzene is formed by the rapid oxidation of hydrazobenzene. Therefore, in these experiments, azobenzene was obtained as the major product and hydrazobenzene as a minor product. UV spectra of these separated products compared well with those of authentic samples. The separated amines were also mixed with *p*-dimethylaminobenzaldehyde and the visible spectra of the resulting derivatives (Zechner *et al* 1976) compared with those of authentic samples. Under these conditions aniline itself, without added peroxydiphosphate, underwent photolysis yielding the same products other than phenylhydroxylamine, but in considerably reduced yields. Experiments were also conducted leaving the reaction mixture in the dark, where it was noticed that the peroxydiphosphate does not oxidise aniline and hence thermal oxidation of aniline by peroxydiphosphate is

of no consequence in our studies. These results show that the greater yield of 4-aminodiphenylamine, azobenzene, benzidine and 2-aminodiphenylamine that are obtained on irradiating the peroxydiphosphate with aniline results from the reaction of the phosphate radical with aniline.

3. Results and discussion

The phosphate radical, PO_4^{2-}·, is produced by the flash photolysis of a deaerated solution containing 1×10^{-5} M peroxydiphosphate at pH 11·0 (Lussier *et al* 1970; Bida *et al* 1973).

$$P_2O_8^{4-} \xrightarrow{h\nu} 2PO_4^{2-}\cdot \tag{1}$$

The absorption of PO_4^{2-}· at 530 nm ($\varepsilon = 2150$ M^{-1} cm^{-1}) (Maruthamuthu and Neta 1978) was observed immediately after the light pulse. The transient absorption spectrum of the phosphate radical at pH 11·0 is shown in figure 1. The flash output energy and the concentration of the peroxydiphosphate were so adjusted as to produce initially 1×10^{-6} M of the phosphate radical. The decay of the radical is second order in the absence of any scavenger as shown in the insert of figure 1 and the decay rate constant (k_r) is 2×10^8 M^{-1} sec^{-1}. This indicates that
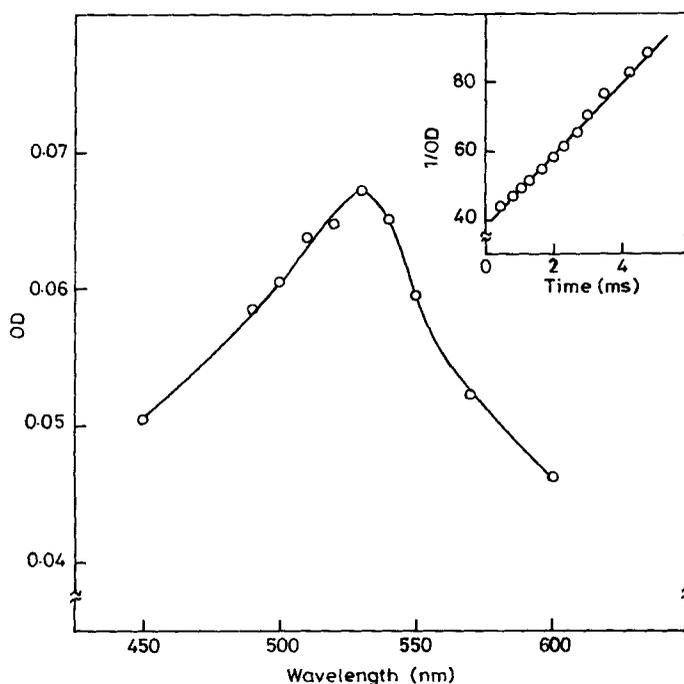

Figure 1. Transient absorption spectrum of phosphate radical produced in the flash photolysis of 0·25 mM peroxydiphosphate at pH 11·0. Optical densities (OD) measured 200 microseconds after start of flash. **Insert:** the second order plot for the decay of phosphate radical at 530 nm.

the disappearance of the radical is largely by a recombination process.

$$2 \text{ PO}_4^{2-\cdot} \xrightarrow{k_r} \text{P}_2\text{O}_8^{4-} \tag{2}$$

In the presence of an excess of amine (scavenger), reaction 3 will compete with the self decay,

$$\text{PO}_4^{2-\cdot} + \text{R}\ddot{\text{N}}\text{H}_2 \xrightarrow{k_s} \text{products.} \tag{3}$$

A pseudo-first order behaviour is observed. This will lead to a composite rate law,

$$-d[\text{PO}_4^{2-\cdot}]/dt = k_s[\text{amine}] \ [\text{PO}_4^{2-\cdot}] + 2k_r[\text{PO}_4^{2-\cdot}]^2. \tag{4}$$

The mixed-order kinetics have been analyzed by the graphic method (Zwicker and Grossweiner 1963) and by computer simulation (Closs and Rabinow 1976). Both of them need the initial concentration of the radical, $[\text{PO}_4^{2-\cdot}]_0$ or initial absorbance (A_0), which involves an element of uncertainty because of the emission of the flash lamp. Nakamura *et al* (1980) attempted to remove the initial concentration of the radical or A_0 from the equation by differentiation with respect to time at an appropriate absorbance A^*; (5) was thus derived,

$$[\text{d } \ln A_t/dt]_{A^*} = -\{k_s[Y^\cdot]_0 + (2k_r'/\varepsilon 1)A^*\}, \tag{5}$$

where $[Y^\cdot]_0$ is the quantity of the scavenger added.

In eqn. 5, the left term is obtained from the tangential line at the appropriate absorbance (A^*) in the first order plot. The slope in the plot of these values against the initial concentration of scavenger yields k_s.

In our studies, the plot of first order rate constants vs [amine] gave a straight line (second order rate constants determined from the slope) passing through the origin indicating that in the presence of excess scavenger the self decay is negligible. The pseudo-first order rate constants were determined for at least three different initial concentrations of scavenger and at each concentration at least three kinetic curves were processed. The second order rate constants (k_s) obtained for some of the aromatic and aliphatic amines are given in table 2. The data are subject to the

Table 2. Rate constants for the reaction of $\text{PO}_4^{2-\cdot}$ radical with amines at pH 11·0 (k_s for $\text{CO}_3^{-\cdot}$ given for comparison).

Amine	$\text{PO}_4^{2-\cdot}$ $k_s(\text{M}^{-1}\,\text{s}^{-1})$	$\text{CO}_3^{-\cdot}$ $k_s(\text{M}^{-1}\,\text{s}^{-1})$
Aniline	$7 \cdot 10 \times 10^8$	$5 \cdot 40 \times 10^8$
	$1 \cdot 47 \times 10^9$ (pH 7·0)[a]	$5 \cdot 50 \times 10^8$ (pH 7·0)
	$\sim 10^{10}$ (pH 5·0)[b]	$5 \cdot 30 \times 10^8$ (pH 5·0)
p-Bromoaniline	$5 \cdot 75 \times 10^8$	$3 \cdot 80 \times 10^8$ (pH 8·5)
p-Aminobenzoic acid	$3 \cdot 12 \times 10^8$	$2 \cdot 00 \times 10^8$ (pH 8·5)
p-Nitroaniline	$1 \cdot 62 \times 10^8$	$7 \cdot 30 \times 10^7$ (pH 8·5)
n-Butylamine	$8 \cdot 68 \times 10^7$	$4 \cdot 00 \times 10^5$
Isopropylamine	$7 \cdot 60 \times 10^7$	$5 \cdot 00 \times 10^5$
Cyclohexylamine	$7 \cdot 77 \times 10^7$	$7 \cdot 20 \times 10^5$
Hexamethylenetetramine	$6 \cdot 04 \times 10^4$	$1 \cdot 70 \times 10^4$

[a] involves $\text{HPO}_4^{-\cdot}$ radical; [b] involves $\text{H}_2\text{PO}_4^{\cdot}$ radical.

errors inherent in flash photolysis studies ($\pm 10\%$). The rate constants for carbonate radical reaction (Elango *et al* 1984, 1985) are given for comparison.

The rate constants, k_s, for aromatic amines are higher than those for aliphatic amines as in the case of the carbonate radical. Hence the reaction pathway of $PO_4^{2-\cdot}$ is likely to be similar to that for $CO_3^{-\cdot}$. The products obtained under conditions of steady state irradiation were the same whether peroxydiphosphate or carbonate were employed as the source of the radical.

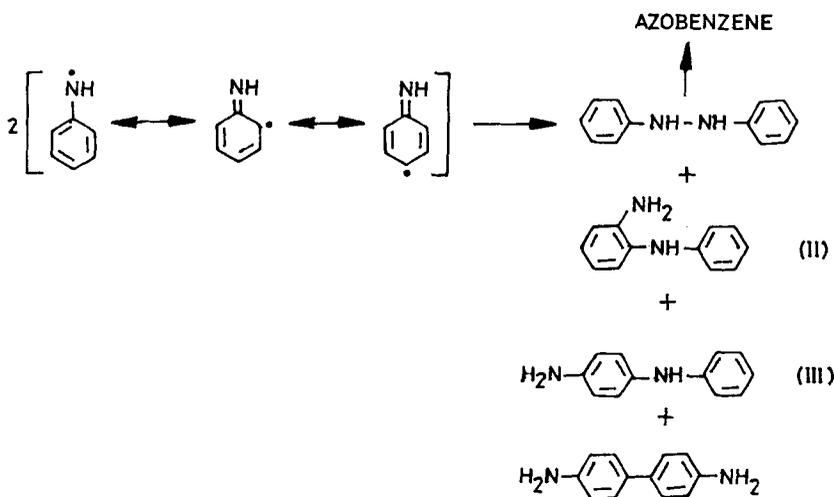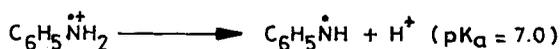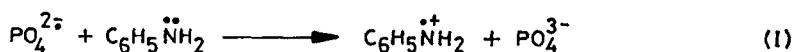## 3.1 *Reaction of phosphate radical with aromatic amines*

The effect of pH on the rate constant for the reaction of phosphate radical with aniline has been studied. The rate constants are markedly different in the pH range 5–11, showing that the intrinsic reactivity of the three forms of phosphate radicals, viz, $H_2PO_4^{\cdot}$, $HPO_4^{-\cdot}$ and $PO_4^{2-\cdot}$, towards aniline is different. However, in the case of the carbonate radical, the rate constants displayed extremely poor dependance on pH showing that the protonated and basic forms of this radical, $HCO_3^{\cdot}$ and $CO_3^{-\cdot}$ respectively, ($pK_a = 9.6 \pm 0.3$) (Cope and Hoffman 1972; Chen *et al* 1973) reacted at the same rate. The carbonate radical reacts with aniline to form an adduct which further dissociates via an electron transfer mechanism (Elango *et al* 1984). According to the theoretical calculations of Eberson (1982), the non-bonded direct electron transfer from aromatic compounds is possible only in the case of the $SO_4^{-\cdot}$ radical and not in the case of OH and $CO_3^{-\cdot}$ radicals. The reactions of phosphate radicals are very similar to that of $SO_4^{-\cdot}$. All these suggest that the reaction of $PO_4^{2-\cdot}$ with aniline is likely to involve a direct electron transfer from aniline to $PO_4^{2-\cdot}$ without adduct formation. Hence attempts have been made to identify the possible anilino-radical intermediate. For the protonated ($C_6H_5\dot{N}^+H_2$) and basic ($C_6H_5\dot{N}H$) forms of the anilino radical, absorption maxima of 423 and 300 nm respectively, have been reported by Land and Porter (1963).

When a solution containing 0·1 mM peroxydiphosphate and 0·1 mM aniline at pH 11·0 is flashed with about 200 J of energy there is very little absorption in the 423 nm region. The absorption around 300 nm could not be followed due to limitations of the monitoring source. But on flashing the same solution with the same energy at pH 6·0, a transient absorption around 424 nm has been observed 1 msec after the start of the flash. This transient absorption is identical with that reported for $C_6H_5\dot{N}^+H_2$ (Land and Porter 1963; Christensen 1972).

Similarly with *p*-nitroaniline at pH 5·0, transient absorption having maxima at 440 and 490 nm was observed. This absorption is due to the formation of the *p*-nitroanilino cation radical, *p*-$NO_2C_6H_4\dot{N}^+H_2$ (Testa and Wollenben 1977). In the absence of peroxydiphosphate, aniline and *p*-nitroaniline showed only very little absorption in these regions. At pH 11·0 the anilino cation radical that is formed probably gets deprotonated to give the anilino radical, $C_6H_5\dot{N}H$ ($pK_a = 7.0$) (Land and Porter 1963), which can further dimerise to give hydrazobenzene and other observed products as shown in the mechanism in scheme 1. In the case of the $CO_3^{-\cdot}$ radical, this scheme is still valid except that step I involves the intermediacy of an adduct.

Due to the resonance structures of anilino radical ($C_6H_5\dot{N}H$) the ortho- and para-positions are active. When two radicals couple, the coupling products can as well arise out of the attack of the NH group of one molecule at the *o*- or *p*- positions

Scheme 1.

$$PO_4^{2-} + C_6H_5\overset{\bullet\bullet}{N}H_2 \longrightarrow C_6H_5\overset{\bullet+}{N}H_2 + PO_4^{3-} \qquad (1)$$

$$C_6H_5\overset{\bullet+}{N}H_2 \longrightarrow C_6H_5\overset{\bullet}{N}H + H^+ \quad (pK_a = 7.0)$$

AZOBENZENE

$$2 \left[\begin{array}{c} \overset{\bullet}{N}H \\ \bigcirc \end{array} \longleftrightarrow \begin{array}{c} NH \\ \bigcirc_\bullet \end{array} \longleftrightarrow \begin{array}{c} NH \\ \bigcirc_\bullet \end{array} \right] \longrightarrow \bigcirc\text{—NH—NH—}\bigcirc$$

$$+$$

$$\bigcirc\overset{NH_2}{\underset{\text{—NH—}}{}}\bigcirc \qquad (II)$$

$$+$$

$$H_2N\text{—}\bigcirc\text{—NH—}\bigcirc \qquad (III)$$

$$+$$

$$H_2N\text{—}\bigcirc\text{—}\bigcirc\text{—}NH_2$$

of the other molecule. Formation of products such as II and III are therefore to be expected.

It would be interesting to compare the reaction of the OH˙ radical (Christensen 1972; Rao and Hayon 1975) and phosphate radical with aniline. The highly reactive OH˙ radical reacts with aniline to give both the cyclohexadienyl type and the anilino radicals. The less reactive $PO_4^{2-\cdot}$ radical is more selective and gives only an anilino radical.

3.2 *Reaction of the phosphate radical with aliphatic amines*

In the case of aliphatic amines there can be two possible mechanisms for the oxidation of amines by one-electron oxidants, which involve (i) direct-electron transfer and (ii) H-atom abstraction as the rate determining steps (Chow 1980; Hull *et al* 1967). Scheme 2 explains these two modes of attack of the $PO_4^{2-\cdot}$ radical on the aliphatic amines.

Both the mechanisms indicate the eventual formation of the same aminoalkyl radical ($R\overset{\cdot}{C}HNR_2'$ or $R\overset{\cdot}{C}HNH_2$). In the electron transfer mechanism this radical is formed by the deprotonation (Anderson and Norman 1971) of aminium cation radical [equation (2) in scheme 2]. The aminoalkyl radical is a strong reducing agent (Anderson and Norman 1971) and readily undergoes oxidation to imine in the presence of mild oxidants present in the solution [(3) and (7)]. Two aminoalkyl radicals can couple (Kumar and Neta 1980) to give an imine, (6), which is readily hydrolysed in the presence of alkali to yield the carbonyl compound as the end
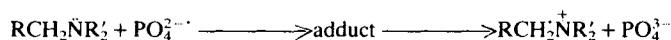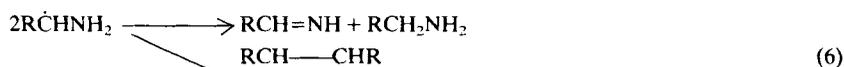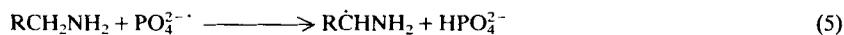
Scheme 2.

(i) a) *Direct one-electron transfer*

$$RCH_2\ddot{N}R_2' + PO_4^{2-\cdot} \longrightarrow RCH_2\dot{N}^+R_2' + PO_4^{3-} \tag{1}$$

$$RCH_2\dot{N}^+R_2' \xrightarrow{-H^+} R\dot{C}HNR_2' \tag{2}$$

$$R\dot{C}HNR_2' \xrightarrow{OX} RCH\overset{+}{=}NR_2' \tag{3}$$

$$RCH\overset{+}{=}NR_2' \xrightarrow{OH^-/H_2O} RCHO + HNR_2' \tag{4}$$

b) *Electron transfer via an adduct*

A variant of (i) (a) is as follows:

$$RCH_2\ddot{N}R_2' + PO_4^{2-\cdot} \longrightarrow adduct \longrightarrow RCH_2\overset{+}{N}R_2' + PO_4^{3-}$$

and steps 2, 3 and 4 as before.

(ii) *α-Hydrogen abstraction*

$$RCH_2NH_2 + PO_4^{2-\cdot} \longrightarrow R\dot{C}HNH_2 + HPO_4^{2-} \tag{5}$$

$$2R\dot{C}HNH_2 \longrightarrow RCH=NH + RCH_2NH_2$$
$$\searrow \quad \underset{NH_2 \quad NH_2}{RCH\!\!-\!\!-\!\!CHR} \tag{6}$$

or

$$R\dot{C}HNH_2 \xrightarrow{OX} RCH=NH \tag{7}$$

$$RCH=NH \xrightarrow{OH^-/H_2O} RCHO + NH_3 \tag{8}$$

Table 3. Products identified in the reaction of $PO_4^{2-\cdot}$ radical with some aliphatic amines.

Amine	Product	Method
n-Butylamine	*n*-Butyraldehyde	by GLC and as 2,4-dinitrophenyl-hydrazone derivative
Cyclohexylamine	Cyclohexanone	by GLC and as 2,4-dinitrophenyl-hydrazone derivative
Di-*n*-propylamine	*n*-Propionaldehyde	as 2,4-dinitrophenyl-hydrazone derivative
Triethylamine	Acetaldehyde	as 2,4-dinitrophenyl-hydrazone derivative

product. The reaction products identified with some of the aliphatic amines are given in table 3.

Detailed studies regarding the mode of attack of $PO_4^{2-\cdot}$ on aliphatic amines and effect of substituent on the reactivity of aniline are in progress.

References

Anderson N H and Norman R O C 1971 *J. Chem. Soc.* B 993

Bida G, Curci R and Edwards J O 1973 *Int. J. Chem. Kinet.* **5** 859

Chen S N, Cope V W and Hoffman M Z 1973 *J. Phys. Chem.* **77** 1111

Chow Y L 1980 *Reaction intermediates* (New York: Plenum) vol. 1, p. 151

Christensen H 1972 *Int. J. Radiat. Phys. Chem.* **4** 311

Closs G L and Rabinow B E 1976 *J. Am. Chem. Soc.* **98** 8190

Cope V W and Hoffman M Z 1972 *Chem. Commun.* 227

Creaser I I and Edwards J O 1972 in *Topics in phosphorus chemistry* (eds) E J Griffith and M Grayson (New York: Wiley Interscience) vol. 7, p. 379

Eberson L 1982 in *Advances in physical organic chemistry* (New York: Academic Press) vol. 18, p. 148

Elango T P, Ramakrishnan V, Vancheesan S and Kuriacose J C 1984 *Proc. Indian Acad. Sci. (Chem. Sci.)* **93** 47

Elango T P, Ramakrishnan V, Vancheesan S and Kuriacose J C 1985 *Tetrahedron* **41** 3837

Hull L A, Davis G T, Rosenblatt D H, Williams H K R and Weglein R C 1967 *J. Am. Chem. Soc.* **89** 1163

Kumar A and Neta P 1980 *J. Am. Chem. Soc.* **102** 7284

Land E J and Porter G 1963 *Trans. Faraday Soc.* **59** 2027

Lussier R J, Risen Jr W M and Edwards J O 1970 *J. Phys. Chem.* **74** 4039

Maruthamuthu P 1974 *Kinetics of oxidation of substrates (oxidation studies involving peroxy diphosphate)* Ph.D. Thesis, Madras University

Maruthamuthu P and Neta P 1977a *J. Phys. Chem.* **81** 937

Maruthamuthu P and Neta P 1977b *J. Phys. Chem.* **81** 1622

Maruthamuthu P and Neta P 1978 *J. Phys. Chem.* **82** 710

Morkovnik A F and Okhlobystein O Yu 1979 *Russ. Chem. Rev. (Engl. Transl.)* **48** 1055

Nakamura M, Ito O and Matsuda M 1980 *J. Am. Chem. Soc.* **102** 698

Rao P S and Hayon E 1975 *J. Phys. Chem.* **79** 1063

Ross A B and Neta P 1979 *National Standard Reference Data Series* (Washington: US Natl. Bur. Stand.) No. 65

Testa A C and Wollenben J 1977 *J. Phys. Chem.* **81** 429

Zechner J, Prangova Lilia St, Grabner G I and Getoff N 1976 *Z. Phys. Chem. (Neue Folge)* **102** 137

Zwicker E F and Grossweiner L I 1963 *J. Phys. Chem.* **67** 549