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Electron Transfer Reactions of Radical Cation and Anion of (R)-(−)-1,1′-Binaphthyl-2,2′-diyl Hydrogen Phosphate in Aqueous Solution. A Pulse Radiolysis Study

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(*R*)-(−)-1,1′-Binaphthyl-2,2′-diyl hydrogen phosphate (BiNPO$_4$H) forms radical anions (λ_{max} = 460 nm and ϵ_{460} = 8600 L mol^{-1} cm^{-1}) on reaction with hydrated electrons. The radical anion undergoes acid-catalyzed protonation with a rate constant of $(5.7 \pm 0.9) \times 10^9$ L mol^{-1} s^{-1} to form H-adduct, which has absorption at λ_{max} = 410 nm. A similar adduct but having a slightly different absorption λ_{max} = 405 nm (ϵ_{405} = 2900 L mol^{-1} cm^{-1}) is formed on the addition of H atoms to BiNPO$_4$H. Addition of OH$^\bullet$ radicals to BiNPO$_4^-$ also formed an adduct which absorbs at λ_{max} = 405 nm (ϵ_{405} = 3100 L mol^{-1} cm^{-1}). Oxidation of BiNPO$_4^-$ with strong oxidizing radicals such as SO$_4^{\bullet-}$, Tl^{2+} and Cl$_2^{\bullet-}$ led to the formation of the radical cation. It is also formed by dehydroxylation of the OH-adduct in acidic solution. The radical cation has a broad absorption spectrum with peaks at 340, 405, 460, and 630 nm (ϵ_{630} = 2000 L mol^{-1} cm^{-1}). It decays with a rate constant of 5×10^4 s^{-1}. Reduction potentials of the radical cation and the anion of BiNPO$_4^-$ have been determined to be 1.70 and −1.51 V vs SHE at pH 9, respectively. The rate constants for electron transfer reactions of these radicals with a number of compounds have been determined as a function of their reduction potentials. The bimolecular rate constants obtained were fitted with the rates predicted by the classical Marcus electron transfer theory. A good free energy gap correlation (log k vs $-\Delta G$) was obtained for the rate constants of reaction of $^{-\bullet}$BiNPO$_4^-$ with organic compounds. The rate constants of reactions of $^{+\bullet}$BiNPO$_4^-$ with inorganic anions also showed a good free energy gap correlation. But rate constants showed poor correlation with the nucleophilicity of the anion. This indicates that reaction between $^{+\bullet}$BiNPO$_4^-$ and inorganic anions is due to electron transfer and not a nucleophilic addition. This was further confirmed from the transient spectrum of the oxidized products formed in the reaction. In contrast to the reaction of the inorganic anions, the rate constants for reaction of $^{+\bullet}$BiNPO$_4^-$ with unsaturated compounds followed the rates predicted by Marcus theory only in the region of $-\Delta G > 0$, and in the $-\Delta G < 0$ region the observed rates are higher than the predicted rates and the deviation from the predicted rate increases with decrease in $-\Delta G$. This indicates that when the electron transfer reaction becomes endothermic, addition of the radical cation to the unsaturated compounds increasingly becomes the dominant pathway of the reaction.

Introduction

Radical anions and cations are key intermediates in many organic syntheses,[1−5] oxidation−reduction reactions, photoinduced electron transfer, and many biological reactions. In photosynthesis the dynamics of the radical ions determines the quantum yield of the process.[6] The radical cation and anion are unstable; they can undergo unimolecular transformations. For example, radical anions may rapidly lose halogen present in the molecule.[7,8] In protic solvents radical anions may rapidly protonate unless they are stabilized by an electron-withdrawing group.[9] Radical anions can transfer electrons to another molecule and can initiate anionic polymerization.[10]

Radical cations are very reactive intermediates. They can undergo C−C bond fragmentation, deprotonation, and isomerization and are easily attacked by a nucleophile.[1−4,11] They can initiate cationic polymerization[12] and undergo intermolecular electron transfer. Due to the susceptibility of the radical cation to nucleophilic attack, aromatic radical cations are not stable in aqueous solution unless they are stabilized by an electron-donating group.[13] For example, a radical cation formed on oxidation of benzene in aqueous solution rapidly undergoes hydrolysis to yield the hydroxycyclohexadienyl radical, whereas radical cations of methoxybenzene and aromatic amines[13,14] have long lifetimes.

There have been a number of studies on the reactions of radical cations with nucleophiles in inert solvents. Reaction of a radical cation with a nucleophile can, in principle, proceed by polar addition and/or electron transfer.[15,17] The relative contribution of the two reaction pathways depends on the radical cation, the nucleophile, and the solvent. The effect of the reactants arises from steric and electronic factors and the redox potentials. Solvent has been reported to have a strong effect on the rate and the reaction mechanism.[17] The rate constants of reaction of a radical cation with nucleophiles such as CN$^-$ and Cl$^-$ differ considerably in acetonitrile and in aqueous acetonitrile. The difference in the rate constants has been attributed to the contribution of hydrogen bonding in aqueous acetonitrile. An interesting case of a change in the mechanism of reaction with the change in solvent has been reported for reaction between azide anion and 4-methoxystyrene radical cation. In acetonitrile, 4-methoxystyrene radical cation reacts with azide anion by electron transfer. In contrast, in 2,2,2-trifluoroethanol it reacts by addition.

As in the case of inorganic nucleophiles, alkenes can react with radical cations by addition and/or electron transfer.[18−20] These reactions are important, as they have synthetic implications. For example, cycloaddition reaction of radical cations to an alkene provides an alternative route to the conventional cyclobutanation and Diels-Alder reactions of neutral substrates.

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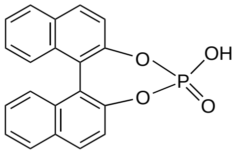
Moreover, these reactions have low activation energy and electron rich dienophiles which are normally unreactive in the conventional Diels-Alder reaction and can conveniently undergo radical cation mediated reaction. Most of the studies on the reaction of radical cations with alkenes are aimed at elucidating their mechanism, and there are only a few reports on the kinetic data.[18−20] Therefore, a kinetic study of the reaction would help in understanding the extent to which the two reaction pathways (addition or electron transfer) contribute in the primary steps of the reaction.

In this work we have chosen (R)-(−)-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate ($BiNPO_4H$) as a model of water soluble aromatic compound to study the reactivities and the mechanism of reaction of the radical ions with different types of compounds. We have also studied the transients formed by reactions of $BiNPO_4H$ with the primary products of water radiolysis (e_{aq}^-, $H^{\bullet}$, and $OH^{\bullet}$). The radical cation of $BiNPO_4^-$ was produced by reaction with specific one-electron oxidants. The bimolecular rate constants of reactions of the radical cation and anion of $BiNPO_4^-$ with different compounds were determined as a function of their redox potentials. The observed rate constants were compared with the rates predicted by classical Marcus theory[21] to determine the contribution of electron transfer in these reactions.



$BiNPO_4H$

Experimental Section

The kinetic spectrophotometric pulse radiolysis apparatus and the associated detection and data processing equipment have been described elsewhere.[8] The dose absorbed by the sample on pulse radiolysis was determined in an aerated 0.05 mol L^{-1} KSCN solution, assuming $G\epsilon = 2.5 \times 10^4$ L mol^{-1} cm^{-1} per 100 eV (*G* is radicals formed per 100 eV). A flow cell of 1.55 cm path length was used for spectral recording. The solutions for pulse radiolysis were adjusted to the desired pH by using $HClO_4$, H_2KPO_4, Na_2HPO_4, and NaOH and were saturated with high-purity N_2, O_2, or N_2O gas prior to the introduction of volatile compounds such as unsaturated compounds into the deaerated solution. Distilled water was further purified in a Millipore Milli-Q system. The bimolecular rate constant *k* for reaction of the reactant radical with a substrate (S) was determined from the slope of the plot of the observed pseudo-first-order rate k_{pseu} vs [S], the substrate S concentration, using the equation

$$k_{pseu} = k_0 + k[S] \qquad (1)$$

In the absence of substrate, k_0^{-1} is the lifetime of the radical in the solution. The uncertainties in the values of *k* were estimated to be 10−20%.[8] (*R*)-(−)-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate ($BiNPO_4H$), 99%, obtained from Aldrich Chemical Co. was used without further purification. All the chemicals used were analytical grade purity or better. The unsaturated compounds were purchased from Aldrich Chemical Co.; they have purity of 98+%.

Results and Discussion

The aromatic compound $BiNPO_4H$ is soluble in water in substantial concentration (4×10^{-3} mol L^{-1}) at pH > 7. It has a $pK_a = 6.5$ (determined by pH titration). Hydrated electrons react with $BiNPO_4^-$ with at rate constant of $(8.5 \pm 1.3) \times 10^9$ L mol^{-1} s^{-1} at pH 7.3.

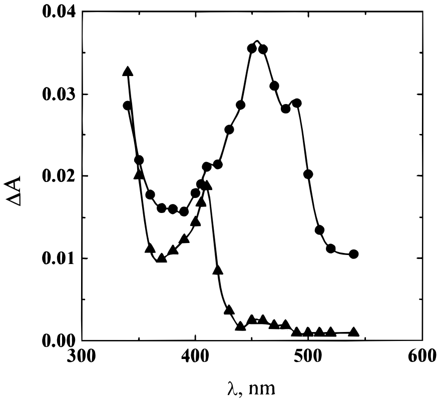


Figure 1. Time-resolved spectra recorded at (●) 1 and (▲) 120 μs showing protonation of the radical anion formed on pulse radiolysis of a deaerated solution of 2.1×10^{-4} mol L^{-1} $BiNPO_4^-$containing 1 mol L^{-1} *t*-BuOH at pH 9.5 (dose = 15 Gy).

$$e_{aq}^- + BiNPO_4^- \rightarrow {}^{-\bullet}BiNPO_4^-$$

The rate constant was determined by monitoring e_{aq}^- decay at 700 nm as a function of $BiNPO_4^-$ concentration in the pulse radiolysis of deaerated solutions of 1 mol L^{-1} 2-methyl-2-propanol (*t*-BuOH). The spectrum (Figure 1) of the radical anion formed recorded at 1 s after pulse radiolysis of a deaerated solution of 2.1×10^{-4} mol L^{-1} $BiNPO_4^-$ and 1 mol L^{-1} *t*-BuOH at pH 9.5 has λ_{max} at 460 nm. It has molar absorptivity[22] at 460 nm of $\epsilon_{460} = 8600$ L mol^{-1} cm^{-1}. The radical anion undergoes acid-catalyzed protonation with a rate constant of $(5.7 \pm 0.9) \times 10^9$ L mol^{-1} s^{-1} to form a H-atom adduct. The

$$H^+ + {}^{-\bullet}BiNPO_4^{\bullet -} \rightarrow HBiNPO_4^-$$

adduct has an absorption maximum λ_{max} at 410 nm. The spectrum of ${}^{\bullet}HBiNPO_4^-$ obtained after the radical anion has decayed resembles the spectrum observed on addition of H atom to $BiNPO_4H$. The spectrum is not due to the dimer radical anion formed by reaction of ${}^{-\bullet}BiNPO_4^-$ with the parent $BiNPO_4^-$. This is indicated by the fact that the decay rate of ${}^{-\bullet}BiNPO_4^-$ at pH 9 changes by <10% as the $BiNPO_4^-$ concentration is varied from 6.5×10^{-5} to 1.3×10^{-3} mol L^{-1}, which yields an upper limit for the reaction of 2×10^6 L mol^{-1} s^{-1}.

H atoms react with $BiNPO_4H$ with a rate constant of $(7.5 \pm 1.1) \times 10^9$ L mol^{-1} s^{-1} at pH 0.5. The rate constant was

$$H^{\bullet} + BiNPO_4H \rightarrow {}^{\bullet}HBiNPO_4H$$

determined by following the formation of the H-adduct at 405 nm as a function of $BiNPO_4^-$ concentration in the pulse radiolysis of deoxygenated solutions of 0.9 mol L^{-1} *t*-BuOH at pH 0.5. The spectrum of the adduct formed recorded at 4 μs after pulse radiolysis of a deoxygenated solution of 2.3×10^{-4} mol L^{-1} $BiNPO_4^-$ containing 0.5 mol L^{-1} *t*-BuOH at pH 0.4 has λ_{max} at 405 nm (Figure 2). It has a molar absorptivity[22] of $\epsilon_{405} = 2900$ L mol^{-1} cm^{-1}. The absorption spectrum obtained on $H^{\bullet}$ addition to $BiNPO_4H$ is more broad than the one obtained on protonation of ${}^{-\bullet}BiNPO_4^-$. This difference may arise from the formation of many isomers of H-adducts produced on addition of $H^{\bullet}$ atoms to different positions of $BiNPO_4^-$, whereas protonation of ${}^{-\bullet}BiNPO_4^-$ may produce predominantly one isomer.

A spectrum similar to that of the H-adduct is obtained on addition of $OH^{\bullet}$ to $BiNPO_4^-$. The rate constant of the addition reaction was determined by following its formation at 405 nm

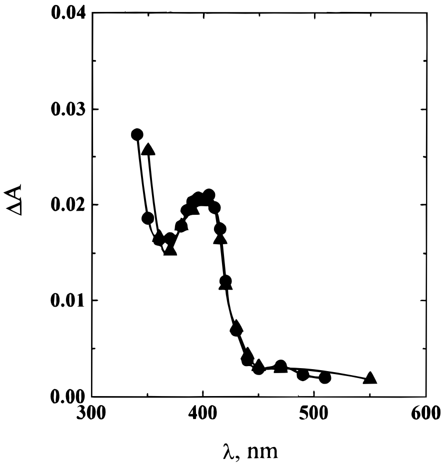


Figure 2. Absorption spectra of H-adduct (●) and of HO-adduct (▲) recorded at 4 and 3 μs after pulse radiolysis, respectively. H-adduct was produced on pulse radiolysis of a deoxygenated solution of 2.3×10^{-4} mol L^{-1} $BiNPO_4^-$ containing 0.5 mol L^{-1} *t*-BuOH at pH 0.4 (dose = 18 Gy), and HO-adduct was produced on pulse radiolysis of an N_2O-saturated solution of 3.6×10^{-4} M $BiNPO_4^-$ at pH 6.9 (dose = 8.0 Gy).

as a function of $BiNPO_4^-$ and was found to be $(1.0 \pm 0.2) \times 10^{10}$ L mol^{-1} s^{-1} at pH 7. The adduct has a spectrum with λ_{max} at 405 nm and $\epsilon_{405} = 3100$ L mol^{-1} cm^{-1}. The spectrum

$$OH^{\bullet} + BiNPO_4^{-} \rightarrow {}^{\bullet}HOBiNPO_4^{-}$$

displayed in Figure 2 was recorded at 3 μs after pulse radiolysis of an N_2O-saturated solution of 3.6×10^{-4} M $BiNPO_4^-$ at pH 6.9.

At pH below 3, the ${}^{\bullet}HOBiNPO_4H$ formed undergoes acid-catalyzed water elimination reaction to form the radical cation ${}^{+\bullet}BiNPO_4^-$. The spectrum of the radical cation has λ_{max} at 340,

$$H^{+} + {}^{\bullet}HOBiNPO_4^{-} \rightarrow {}^{+\bullet}BiNPO_4^{-} + H_2O$$

405, 460, and 630 nm. The radical cation ${}^{+\bullet}BiNPO_4^-$ is also formed upon oxidation of $BiNPO_4^-$ by $SO_4^{\bullet-}$. The oxidation reaction has a rate constant of $(1.4 \pm 0.2) \times 10^{10}$ L mol^{-1} s^{-1}, as determined by following the formation of ${}^{+\bullet}BiNPO_4^-$ at 630 nm as a function of $BiNPO_4^-$ concentration in the pulse radiolysis of deoxygenated solutions of 0.05 mol L^{-1} $S_2O_8^{2-}$

$$e_{aq}^{-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{\bullet-}$$

$$SO_4^{\bullet-} + BiNPO_4^{-} \rightarrow SO_4^{2-} + {}^{+\bullet}BiNPO_4^{-}$$

and 0.08 mol L^{-1} *t*-BuOH at pH 9.4. The spectrum of the radical cation ${}^{+\bullet}BiNPO_4^-$ (Figure 3) recorded at 3 μs after pulse radiolysis of a deoxygenated solution of 2.0×10^{-4} mol L^{-1} $BiNPO_4^-$ containing 0.05 mol L^{-1} $K_2S_2O_8$ and 0.19 mol L^{-1} *t*-BuOH at pH 7.3 has λ_{max} at 340, 405, 460, and 630 nm. A number of other specific one-electron oxidants such as Tl^{2+} and $Cl_2^{\bullet-}$ also oxidize $BiNPO_4^-$ with rate constants of $(1.5 \pm 0.2) \times 10^9$ at pH 3.3 and $(7.4 \pm 1.1) \times 10^8$ L mol^{-1} s^{-1} at pH 2.7, respectively (Table 1). The radical cation has a molar absorptivity[23] at 630 nm of $\epsilon_{630} = 2000$ L mol^{-1} cm^{-1}. It decays with a rate constant of 5×10^4 s^{-1}. The decay may be partly due to reaction with the precursor and hydrolysis of the radical cation. By changing the concentration of $BiNPO_4^-$ by a factor of 10 from 1.3×10^{-4} to 1.3×10^{-3} mol L^{-1}, the decay rate changes by <10% and yields an upper limit of 3×10^6 L mol^{-1} s^{-1} for the rate of reaction of the radical cation with its precursor.

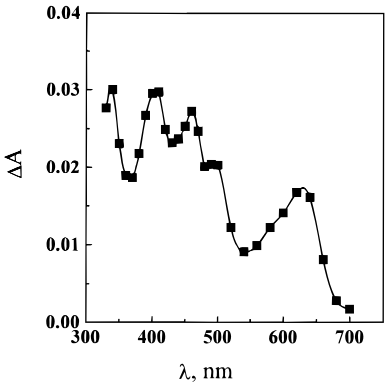


Figure 3. Absorption spectrum of the radical cation ${}^{+\bullet}BiNPO_4^-$ recorded at 3 μs after pulse radiolysis of a deoxygenated solution of 2.0×10^{-4} mol L^{-1} $BiNPO_4^-$ containing 0.05 mol L^{-1} $K_2S_2O_8$ and 0.19 mol L^{-1} *t*-BuOH at pH 7.3 (dose = 18 Gy).

TABLE 1: Bimolecular Rate Constants for Reactions of $BiNPO_4^-$ with Different Radicals

radical	compound	pH	*k*, L mol^{-1} s^{-1}
e_{aq}^-	$BiNPO_4^-$	7.3	$(8.5 \pm 1.3) \times 10^9$
$H^{\bullet}$	$BiNPO_4^-$	0.5	$(7.5 \pm 1.1) \times 10^9$
$OH^{\bullet}$	$BiNPO_4^-$	7	$(1.0 \pm 0.1) \times 10^{10}$
$Cl_2^{\bullet-}$	$BiNPO_4^-$	2.7	$(7.4 \pm 1.1) \times 10^8$
Tl^{2+}	$BiNPO_4^-$	3.3	$(1.6 \pm 0.2) \times 10^9$
$SO_4^{\bullet-}$	$BiNPO_4^-$	9.4	$(1.4 \pm 0.2) \times 10^{10}$
${}^{-\bullet}BiNPO_4^-$	H^+		$(5.7 \pm 0.9) \times 10^{9)}$

SCHEME 1

$$D^{\bullet-} + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} D + A^{\bullet-}$$

Redox Potentials of $BiNPO_4^-$. For a redox reaction between D and A in Scheme 1, the observed rate k_{obs} of approach of equilibrium is related to the rates of forward k_1 and reverse k_{-1}.[24]

$$k_{obs} = k_1[A] + k_{-1}[D] \tag{2}$$

In this study, ${}^{-\bullet}BiNPO_4^-$ is the donor $D^{\bullet-}$ in reduction reactions and ${}^{+\bullet}BiNPO_4^-$ is the acceptor $A^{\bullet+}$ in oxidation reactions. The reduction potentials of D and A are related to the equilibrium constant *K* by eq 3.

$$\Delta E = E(A/A^{\bullet-}) - E(D/D^{\bullet-}) = 0.0591 \log K \tag{3}$$

To make sure that the k_{obs} measures the rate of approach to the equilibrium in eq 2, k_{obs} is maintained at a much higher rate than the rate of decay of the radical monitored by adjusting the concentration of the reactants. To maintain the equilibrium constant within a reasonable value, the reduction potential of the reference couple is kept within ~0.1 V of the expected redox potential.

Figure 4 shows a plot of $k_{obs}/[C_6H_5CN]$ vs $[(CH_3)_2CO]/[C_6H_5CN]$ for electron transfer reaction between acetone and benzonitrile at pH 9. The plot yields an equilibrium constant of $K = 0.18$ and a reduction potential of $E(C_6H_5CN/C_6H_5CN^{\bullet-}) = -1.45$ V vs SHE at pH 9 using $E[(CH_3)_2CO/(CH_3)_2CO^{\bullet-}] = -1.5$ V[25] as the reference potential. In a similar plot (Figure 4) a reduction potential of −1.48 V vs SHE at pH 9 was obtained as the reduction potential of the $C_6H_5COCH_3/C_6H_5COCH_3^{\bullet-}$ couple. Using $E(C_6H_5CN/C_6H_5CN^{\bullet-}) = -1.45$ V as the reference couple, the reduction potential of $BiNPO_4^-$ was determined from the reaction

$${}^{-\bullet}BiNPO_4^{-} + C_6H_5CN \rightleftharpoons BiNPO_4^{-} + C_6H_5CN^{\bullet-}$$

The observed rate k_{obs} was determined by following the decay of ${}^{-\bullet}BiNPO_4^-$ absorption at 460 nm as a function of C_6H_5CN concentration in the pulse radiolysis of a deoxygenated solution

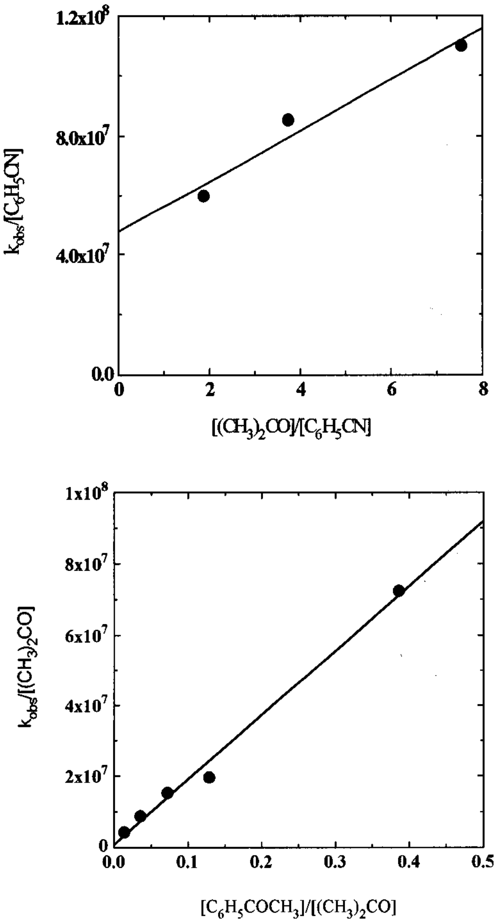


Figure 4. Plots of $k_{obs}/[C_6H_5CN]$ vs $[(CH_3)_2CO]/[C_6H_5CN])]$ and $k_{obs}/[(CH_3)_2CO]$ vs $[C_6H_5COCH_3)]/[(CH_3)_2CO]$ for determination of reduction potentials.

SCHEME 2

$$D + A \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} [D\cdots A] \xrightarrow{k_{et}} D^{\bullet +} + A^{\bullet -}$$

of 9.6×10^{-4} mol L^{-1} $BiNPO_4^-$ solution containing 0.3 mol L^{-1} *t*-BuOH at pH 9. A plot of $k_{obs}/[BiNPO_4^-]$ vs $[C_6H_5CN]/[BiNPO_4^-]$ in Figure 5 yields an equilibrium constant of $K = 10.6$ and a reduction potential $E(BiNPO_4^-/^{-\bullet}BiNPO_4^-) = -1.51$ V vs SHE at pH 9.

The oxidation potential of $BiNPO_4^-$ was determined from reaction with SeO_3^{2-}. The observed rate k_{obs} was determined

$$SeO_3^{2-} + {}^{+\bullet}BiNPO_4^- \rightleftharpoons BiNPO_4^- + SeO_3^{\bullet -}$$

by following the decay of ${}^{+\bullet}BiNPO_4^-$ at 630 nm as a function of SeO_3^{2-} concentration in the pulse radiolysis of a deaerated solution of 1×10^{-3} mol L^{-1} $BiNPO_4^-$ containing 0.05 mol L^{-1} $S_2O_8^{2-}$ and 0.08 mol L^{-1} *t*-BuOH at pH 9. A plot of $k_{obs}/[BiNPO_4^-]$ vs $[SeO_3^{2-}]/[BiNPO_4^-]$ as shown in Figure 5 yields $K = 1.91$ and a reduction potential of $E({}^{+\bullet}BiNPO_4^-/BiNPO_4^-) = 1.70$ V vs SHE at pH 9 using $E(SeO_3^{\bullet -}/SeO_3^{2-}) = 1.68$ V[26] vs SHE as reference.

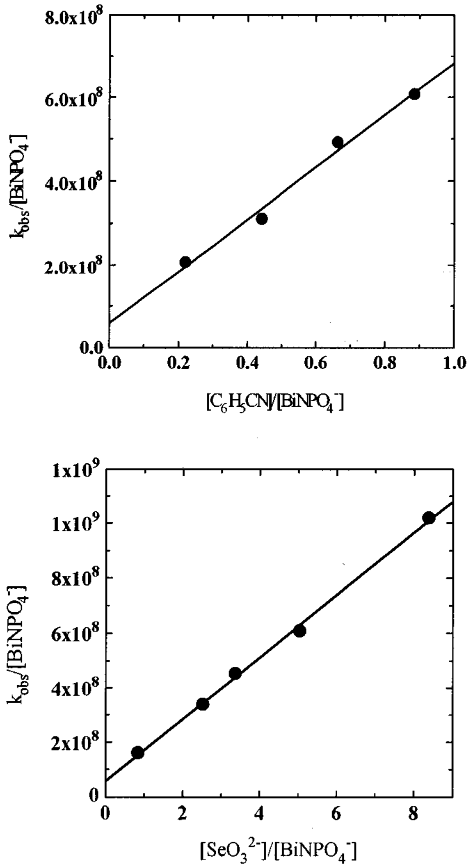


Figure 5. Plots of $k_{obs}/[BiNPO_4^-]$ vs $[C_6H_5CN)]/[BiNPO_4^-]$ and $k_{obs}/[BiNPO_4^-]$ vs $[SeO_3^{2-}]/[BiNPO_4^-]$ for determination of reduction potentials.

Energy Gap Dependence of Bimolecular Electron Transfer Rate Constants. The kinetics of the electron transfer reaction is presented in Scheme 2. Here the donor D and the acceptor A diffuse together with a rate k_d to form an encounter complex which undergoes electron transfer with a rate k_{et}. The encounter complex dissociates with a rate k_{-d}. By applying a steady state approximation the expression for the measured bimolecular rate constant *k* is given by[27,28]

$$\mathrm{k} = \frac{k_d}{1 + \dfrac{k_{-d}}{k_{et}}} = \frac{k_d}{1 + \dfrac{k_d}{k_{et}}\dfrac{k_{-d}}{k_d}} \tag{4}$$

For simplicity $k_d/k_{-d} = 1$ L mol^{-1} is assumed,[21] and in aqueous solution $k_d = 8.02 \times 10^9$ L mol^{-1} s^{-1} at 28 °C.

The expression correlating the bimolecular rate constant and the free energy gap dependence for outer-sphere electron transfer in the weak coupling limit is given by the classical Marcus theory.[21,27,28]

$$k = \frac{k_d}{1 + \dfrac{k_{-d}}{k_{max}} \exp\left[\dfrac{\Delta G_c^{\ddagger}}{RT} + \dfrac{(\lambda + \Delta G^\circ)^2}{4\lambda RT}\right]} \tag{5}$$

where the terms have the standard meaning; k_{max} is the maximum electron transfer rate for barrierless electron transfer normally assumed to be 10^{13} s^{-1}. When either one of the reactants is uncharged, $\Delta G_c^{\ddagger} = 0$ and the standard free energy difference is given by

$$\Delta G^\circ = E_{ox} - E_{red} \tag{6}$$

For electron transfer reaction between two charged species, ΔG° is given by eq 7.[29]

$$\Delta G^\circ = E_{ox} - E_{red} + (Z_1 - Z_2 - 1)\frac{e^2}{\epsilon r_{DA}} \tag{7}$$

where Z_1 and Z_2 are the charges on the donor and the acceptor, respectively. The reorganization energy is the sum of the

TABLE 2: Bimolecular Electron Transfer Reactions of $^{-\bullet}$BiNPO$_4^-$ with Different Compounds

compound	pH	$E_{1/2}$/V[24]	$-\Delta G°$, kcal mol^{-1}	k, L mol^{-1} s^{-1}
Q	9.5	0.099	37.10	$(6.0 \pm 0.9) \times 10^9$
MV^{2+}	9.2	−0.444	27.35	$(8.0 \pm 1.2) \times 10^9$
C_6F_5CHO	9.0	−0.75[8]	17.53	$(3.4 \pm 0.5) \times 10^9$
2,2-bipyridyl	9.0	−0.97[33]	12.45	$(4.9 \pm 0.7) \times 10^9$
$C_6H_5COCH_3$	11.4	−1.36	3.46	$(5.0 \pm 0.8) \times 10^9$
C_6H_5CN	9.0	−1.45	1.38	$(6.2 \pm 0.9) \times 10^8$
CH_3COCH_3	9.0	−1.50[25]	0.23	$(2.3 \pm 0.3) \times 10^7$

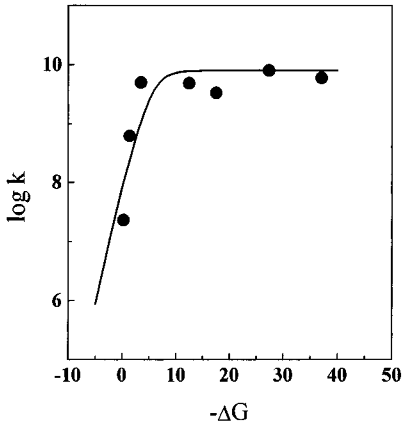


Figure 6. Energy gap dependence of the bimolecular rate constants for reaction of $^{-\bullet}$BiNPO$_4^-$ with organic compounds in aqueous solution. The theoretical curve was calculated from eq 5 with the fitting parameters $\Delta G_c^\ddagger = 0$ and $\lambda = 28$ kcal mol^{-1} (calculated value using eq 8 yields $\lambda_0 = 24.4$ kcal mol^{-1}).

contribution from the vibrational (λ_i) and solvent reorganization (λ_0). Solvent reorganization energy λ_0 can be easily evaluated from the van der Waals radii[30] r_D and r_A using eq 8.

$$\lambda_0 = e^2\left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r_{DA}}\right)\left(\frac{1}{n^2} - \frac{1}{\epsilon}\right) \tag{8}$$

The electrostatic free energy change $\Delta G_c^\ddagger$ required to bring the two charged species to their reaction distance r_{DA} in the collision complex in a medium of dielectric constant ϵ and ionic strength μ is given by eq 9.[27,28]

$$\Delta G_c^\ddagger = \frac{Z_1 Z_2 e^2}{\epsilon r_{DA}} \exp\left(-r_{DA}\left[\frac{8\pi e^2 N_0 \mu}{1000\epsilon k_B T}\right]^{1/2}\right) \tag{9}$$

Here, e is the electronic charge, N_0 is the Avogadro number, and k_b is the Boltzmann constant. In a typical reaction between $^{+\bullet}$BiNPO$_4^-$ and N_3^- in a solution of ionic strength $\mu = 0.14$ M, $\Delta G^\ddagger = 0.35$ kcal mol^{-1}.

Electron Transfer Reactions $^{-\bullet}$BiNPO$_4^-$ with Organic Compounds. The rate constants for reduction of different organic compounds by $^{-\bullet}$BiNPO$_4^-$ are summarized in Table 2. They were determined from the slope of the plot of k_{pseu} vs [S] (eq 1). The pseudo-first-order decay rate was determined by monitoring the decay of $^{-\bullet}$BiNPO$_4^-$ at 460 nm as a function of substrate concentration in pulse radiolysis of a deoxygenated solution of 7×10^{-4} mol L^{-1} BiNPO$_4^-$ containing 0.5 mol L^{-1} *t*-BuOH. Reactions of $^{-\bullet}$BiNPO$_4^-$ with 2,2′-bipyridyl and MV^{2+} were monitored at 350 and 605 nm, respectively. For a reaction involving neutral reactants the Coulomb term $\Delta G_c^\ddagger = 0$, and for reaction between $^{-\bullet}$BiNPO$_4^-$ and MV^{2+} in a solution of ionic strength $\mu = 0.01$ mol L^{-1}, $G_c^\ddagger = -1.7$ kcal mol^{-1} (calculated from eq 9). A plot of the dependence of the bimolecular rate constants on $-\Delta G°$ is shown in Figure 6. The experimental points were fitted with the rates predicted by Marcus equation 5. A reasonably good fit was obtained with $\lambda = 28$ kcal mol^{-1}, indicating that the rate constants are due to electron transfer. This was confirmed from the transient spectrum of the product formed in the reaction. It is interesting to note that λ obtained from the fitted curve is very similar in magnitude to the value of $\lambda_0 = 24.4$ kcal mol^{-1} calculated from van der Waals radii[30] using eq 8. This indicates that most of the reorganization energy of the reaction comes from the solvent reorganization, and vibrational reorganization λ_i is small as expected for an aromatic system.[21,27,28]

TABLE 3: Bimolecular Rate Constants for Electron Transfer Reactions of $^{+\bullet}$BiNPO$_4^-$ with Inorganic Anions

anion	pH	$E_{1/2}$/V[26]	$-\Delta G°$, kcal mol^{-1}	k, L mol^{-1} s^{-1}
NO_2^-	9.4	1.04	17.27	$(2.8 \pm 0.4) \times 10^9$
N_3^-	9.5	1.33	10.58	$(6.4 \pm 1.0) \times 10^9$
I^-	8.6	1.33	10.58	$(5.4 \pm 0.8) \times 10^9$
SCN^-	8.4	1.63	3.66	$(2.5 \pm 0.4) \times 10^9$
SeO_3^{2-}	9.4	1.68	3.19	$(1.1 \pm 0.2) \times 10^8$
Br^-	8.6	1.92	−3.03	$(2.5 \pm 0.4) \times 10^6$

Reactions of $^{+\bullet}$BiNPO$_4^-$ with Inorganic Anions. A radical cation can react with an anionic nucleophile by addition and/or electron transfer.[1−4,15−17] Solvent polarity and redox potential of the nucleophile have a strong effect on the relative contributions of the two pathways. An aromatic radical cation reacts with amines by either addition or electron transfer depending on the reduction potential of the amines.[16] It also react with inorganic anions by addition and electron transfer.[15] Interestingly its reaction with azide anion exhibits strong solvent dependence. In acetonitrile it undergoes electron transfer, whereas in 1,1,1-trifluoroethanol or aqueous acetonitrile as solvents it reacts by addition.[17] In order to elucidate the reaction mechanism of an aromatic radical cation with an inorganic anion in aqueous solution, we have determined several bimolecular rate constants for reaction of $^{+\bullet}$BiNPO$_4^-$ with different inorganic anions. The rate constants were determined by using eq 1. The pseudo-first order decay rate k_{pseu} was determined by following the decay of $^{+\bullet}$BiNPO$_4^-$ at 630 or 460 nm as a function of anion concentration in pulse radiolysis of a deoxygenated solution of 1×10^{-3} mol L^{-1} BiNPO$_4^-$ containing 0.05 mol L^{-1} $S_2O_8^{2-}$ and 0.1 mol L^{-1} *t*-BuOH (NaOH was added to bring the solution to pH 9). The rate constants determined are summarized in Table 3.

$$N_3^- + {}^{+\bullet}BiNPO_4^- \rightarrow N_3^\bullet + BiNPO_4^-$$

$$N_3^- + {}^{+\bullet}BiNPO_4^- \rightarrow N_3^\bullet BiNPO_4^-$$

For a singly charged inorganic anion in aqueous solution of ionic strength $\mu = 0.16$ mol L^{-1}, eq 9 yields an electrostatic free energy of $\Delta G^\ddagger = -0.35$ kcal mol^{-1}. This parameter in the Marcus equation was included in fitting the experimental rate constants to determine the contribution of electron transfer in the reaction. The experimental points can be fitted reasonably well with a reorganization energy of $\lambda = 31$ kcal mol^{-1}, as shown in Figure 7, thereby indicating that the reactions are due to electron transfer. This was further confirmed from the time-resolved spectrum of the product formed in the reaction; for example

$$SCN^- + {}^{+\bullet}BiNPO_4^- \rightarrow SCN^\bullet + BiNPO_4^-$$

$$SCN^- + SCN^\bullet \rightarrow (SCN)_2^{\bullet -}$$

Figure 8 shows the spectra recorded at different times after pulse radiolysis of a deoxygenated solution containing 3.1×10^{-4} mol L^{-1} BiNPO$_4^-$, 7.9×10^{-5} mol L^{-1} SCN$^-$, 0.06 mol L^{-1} $S_2O_8^{2-}$, and 0.09 mol L^{-1} *t*-BuOH at pH 9. The time-resolved spectra clearly showed the evolution of the initially formed

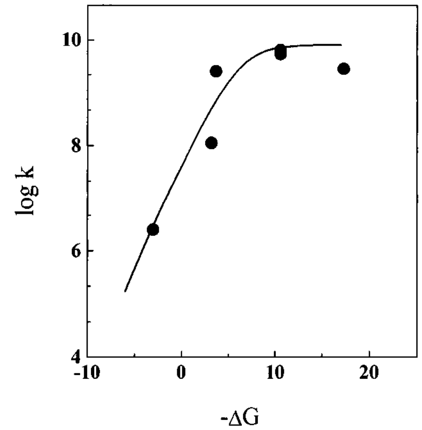


Figure 7. Energy gap dependence of the bimolecular rate constants for reaction of $^{+\bullet}BiNPO_4^-$ with inorganic anions in aqueous solution. The theoretical curve was calculated from eq 5 with fitting parameters (a) $\Delta G_c^\ddagger = -0.35$ kcal mol^{-1} and $\lambda = 31$ kcal mol^{-1} (calculated value using eq 8 yields $\lambda_0 = 38.2$ kcal mol^{-1}).

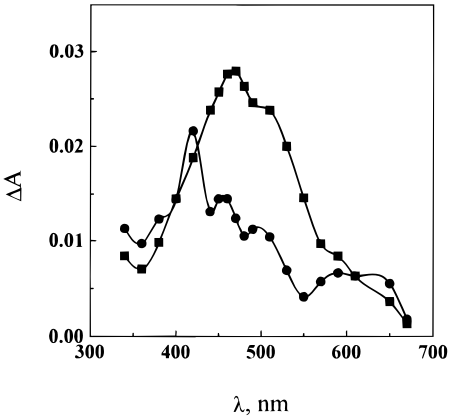


Figure 8. Time-resolved spectra recorded at (●) 0.4 and (■) 8.4 μs showing decay of $^{+\bullet}BiNPO_4^-$ and formation of $(SCN)_2^{\bullet-}$ absorption on pulse radiolysis of a deoxygenated solution containing 3.1×10^{-4} mol L^{-1} $BiNPO_4^-$, 7.9×10^{-5} mol L^{-1} SCN^-, 0.06 mol L^{-1} $S_2O_8^{2-}$, and 0.09 mol L^{-1} t-BuOH at pH 9.

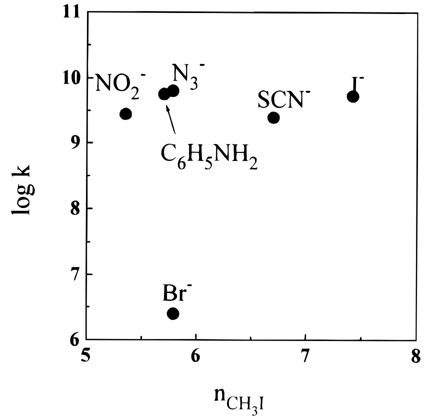


Figure 9. Dependence of the bimolecular rate constants on nucleophilicity of the inorganic anion in aqueous solution.

$^{+\bullet}BiNPO_4^-$ spectrum to that of $(SCN)_2^{\bullet-}$ as a consequence of electron transfer reaction. Evidence for the lack of nucleophilic addition in these reactions was obtained from the plot of log k vs n_{CH3I}, the nucleophilicity of the anions[31] as presented in Figure 9. The plot shows that the rates are insensitive to the nucleophilicity of the anion. Even for anions having very similar nucleophilicity, as in the case of Br^- and N_3^-, their rate constants differ by a factor of 1000. This difference in the rate constants can however be very well accounted for by the difference in their redox potentials.

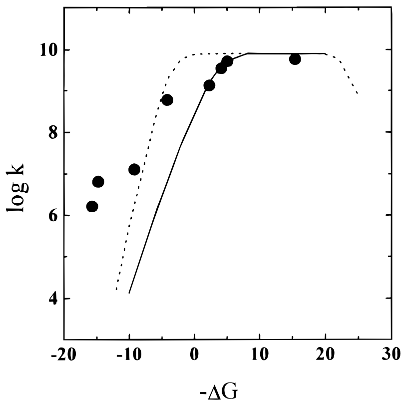


Figure 10. Energy gap dependence of the bimolecular rate constants of reaction of $^{+\bullet}BiNPO_4^-$ with unsaturated compounds in aqueous solution. The theoretical curves were calculated from eq 5 with the fitting parameters $\Delta G_c^\ddagger = 0$ and $\lambda = 10$ kcal mol^{-1} (···) and $\Delta G_c^\ddagger = 0$ and $\lambda = 24.8$ kcal mol^{-1} (—) (calculated value using eq 8 yields $\lambda_0 = 24.9$ kcal mol^{-1}).

Reaction of $^{+\bullet}BiNPO_4^-$ with Unsaturated Compounds. Reactions of radical cations with alkenes normally lead to the formation of adducts such as cyclobutane and Diels-Alder products.[1−4,17−20] A number of factors such as steric and electronic effects, reduction potential, and solvent have strong influence on the reaction mechamism.

$$^{+\bullet}BiNPO_4^- + \| \rightarrow \text{adduct}$$

$$^{+\bullet}BiNPO_4^- + \| \rightarrow BiNPO_4^- + \|^{\bullet+}$$

Electron transfer can compete with the synthetically useful adduct formation when the difference in the redox potential is favorable. Solvent has a strong effect on the reaction mechanism. Polar solvent favors electron transfer, but polar hydrogen bond donating solvent favors adduct formation.

In aqueous solution the radical cations of $BiNPO_4^-$ were generated by oxidation reaction with $SO_4^{\bullet-}$. The rate constants for reaction of $^{+\bullet}BiNPO_4^-$ with unsaturated compounds were determined from the dependence of the decay rate of the radical cation monitored at 460 nm on the concentration of unsaturated compound in the pulse radiolysis of deoxygenated buffered solution containing 1.1×10^{-3} mol L^{-1} $BiNPO_4^-$, 0.04 mol L^{-1} $S_2O_8^{2-}$, and 0.1 mol L^{-1} t-BuOH. The rate constants determined are summarized in Table 4.

The dependence of the experimentally determined rate constants on the free energy change $\Delta G°$ for electron transfer reactions is shown in Figure 10. It is seen that the experimental points do not fit the Marcus equation. The fitted curve with a reorganization energy of $\lambda = 24.8$ kcal mol^{-1} can account for some of the experimentally observed rates which are close to diffusion controlled rates. The curves fitted with lower reorganization energies increase the deviation from the experimental points, as shown for example for a curve fitted with $\lambda = 10$ kcal mol^{-1}. The Marcus relation tells us that for an electron transfer reaction a plot of log k vs $\Delta G°$ should have a slope of $1/2.303RT$ (17 eV^{-1}) in the region $\Delta G° > \lambda$ and a slope of $>0.5/2.303RT$ (8.4 eV^{-1}) in the region $\Delta G° > \lambda/4$. The calculated Marcus curve for the log k vs $\Delta G°$ plot has in the region of $\Delta G° > \lambda/4$ a slope of 13.9 and 8.9 eV^{-1} for a reorganization energy of 10 and 24.8 kcal mol^{-1}, respectively. The experimentally observed log k vs $\Delta G°$ plot has a slope of 4.5 eV^{-1} in the region of $\Delta G° > 6$ kcal mol^{-1}. It can be seen that the experimentally observed slope is much smaller than the slope predicted by the Marcus relation. This shows that electron transfer reaction contributes little or is negligible in

TABLE 4: Bimolecular Rate Constants for Reaction of $^{+\bullet}\mathrm{BiNPO_4}^-$ with Unsaturated Compounds

unsaturated compound	pH	$E_{1/2}$/V^{34}	$\Delta G°$, kcal mol^{-1}	k, L mol^{-1} s^{-1}
aniline	8.3	1.03	15.45	$(5.8 \pm 0.9) \times 10^9$
pyrrole	8.9	1.48	5.07	$(5.2 \pm 0.8) \times 10^9$
2,5-dimethylfuran	8.5	1.52	4.15	$(3.5 \pm 0.5) \times 10^9$
3,4-dihydro-2-methoxy-2*H*-pyran	8.5	1.60	2.31	$(1.3 \pm 0.2) \times 10^9$
2-methoxypropene	8.5	1.88	−4.15	$(5.9 \pm 0.9) \times 10^8$
furan	8.3	2.10	−9.22	$(1.3 \pm 0.2) \times 10^7$
2,5-dimethoxy-2,5-dihydrofuran	9.6	2.34	−14.76	$(6.5 \pm 1.0) \times 10^6$
vinyl acetate	8.3	2.38	−15.68	$(1.6 \pm 0.3) \times 10^6$

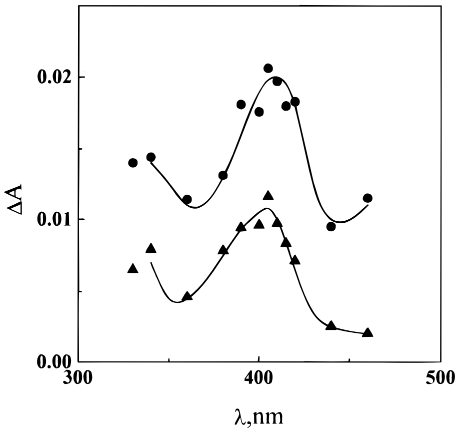


Figure 11. Time-resolved spectra recorded at (●) 1 μs and (▲) 20 μs showing the formation of adduct on pulse radiolysis of a deoxygenated solution of 1.5×10^{-3} mol L^{-1} BiNPO$_4^-$ containing 1.5×10^{-3} mol L^{-1} 2-methoxypropene, 0.03 mol L^{-1} $S_2O_8^{2-}$, and 0.1 mol L^{-1} *t*-BuOH at pH 9.2.

the region of $\Delta G° > 0$, and this indicates that the reaction must be due to adduct formation. The formation of adduct in this reaction is also indicated by the transient spectrum obtained in the reaction for example between $^{+\bullet}$BiNPO$_4^-$ and 2-methoxypropene. The spectrum obtained (Figure 11) is similar to that

$$^{+\bullet}\mathrm{BiNPO_4}^- + \mathrm{CH_3(CH_3O)C{=}CH_2} \rightarrow \text{adduct}$$

of the H- or HO-radical adduct of BiNPO$_4^-$, indicating that the radical cation adds to the double bond of the unsaturated compound. The difference between the observed and the fitted curve with $\lambda = 24.8$ kcal mol^{-1} indicates that adduct formation dominates its reactions with furan, 2,5-dimethoxy-2,5-dihydrofuran, and vinyl acetate. However, for reactions for which electron transfer is exothermic, electron transfer can be expected to compete with addition or it may even dominate the reaction. This is demonstrated in the reaction between $^{+\bullet}$BiNPO$_4^-$ and aniline, where the rate constant is diffusion controlled as

$$^{+\bullet}\mathrm{BiNPO_4}^- + \mathrm{C_6H_5NH_2} \rightarrow \mathrm{BiNPO_4}^- + \mathrm{C_6H_5NH_2}^{\bullet+}$$

$$\mathrm{C_6H_5NH_2}^{\bullet+} \xrightleftharpoons{pK_a = 7.0} \mathrm{C_6H_5NH}^{\bullet} + \mathrm{H}^+$$

predicted by Marcus theory, and the transient observed after the decay of $^{+\bullet}$BiNPO$_4^-$ has a spectrum that can be identified with the anilino radical[14] with $\lambda_{max} = 400$ nm (Figure 12). The results of the studies on the reaction between the radical cation of BiNPO$_4^-$ and unsaturated compounds in aqueous solution indicate that the reaction can proceed via both addition and electron transfer. In the region where electron transfer is exothermic electron transfer reaction predominates, whereas in the endothermic region the reaction follows the alternative route to form adduct. In the intermediate region it is possible that both pathways compete; however, we did not make any attempt to determine the relative contribution.

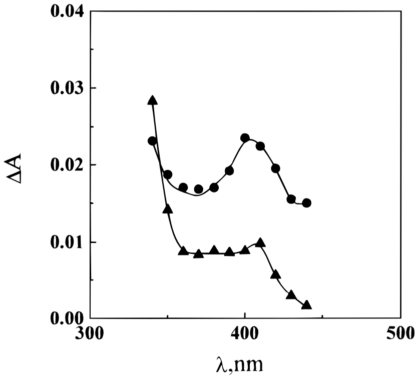


Figure 12. Time-resolved spectra recorded at (●) 1 μs and (▲) 5 μs showing the formation of anilino-radical ($\epsilon_{400} = 1300$ L mol^{-1} cm^{-1})[14] on pulse radiolysis of a deoxygenated solution of 8.5×10^{-4} mol L^{-1} BiNPO$_4^-$ containing 2.7×10^{-4} mol L^{-1} aniline, 0.06 mol L^{-1} $S_2O_8^{2-}$, and 0.1 mol L^{-1} *t*-BuOH at pH 9.2.

It is appropriate to comment about the reorganization energy of the reaction. A reorganization energy of 24.8 kcal mol^{-1} obtained for the best fit of the curve is similar to the solvent reorganization energy $\lambda_0 = 24.9$ kcal mol^{-1} calculated from the radii of the reactants using eq 8. The agreement probably may not be fortuitous, because the product unsaturated radical cation formed can be stabilized by the heteroatom present in the molecule, thereby imparting substantial positive charge on the heteroatom. This picture of electron transfer reaction would require substantial solvent reorganization energy and may even dominate the overall reorganization energy of the reaction. The same reasoning can be made for electron transfer reaction between the radical anion $^{-\bullet}$BiNPO$_4^-$ and organic compounds studied here. Although solvent reorganization energy may be relatively small for $^{-\bullet}$BiNPO$_4^-$, as the unpaired spin density is expected to be delocalized within the aromatic chromophore, the solvation reorganization energy may be quite substantial for the radical anions of acetone, acetophenone, and acetonitrile. In these radical anions the excess electron is localized mainly on the heteroatom. It is also seen that the experimental points are fitted well with $\lambda = 28$ kcal mol^{-1}, which is close the λ_0 (24.4 kcals mol^{-1}) calculated from eq 8. Similar observations have been reported for electron transfer reactions involving radical cations and anions of some aromatic compounds where vibrational reorganization energy accounts for less than 10% of the total reorganization energy.[21,27,28] However, it should noted that λ_0 calculated from van der Waals radii are often much higher than the experimental value.

Conclusion

The radical anion and cation of BiNPO$_4^-$ have been generated in aqueous solution by pulse radiolysis, and the mechanism of their reactions with different reactants has been studied. The radical anion reacts with electron affinic compounds by electron transfer. It also undergoes acid-catalyzed protonation in aqueous solution. The reaction of the radical cation with inorganic anions has been shown to be electron transfer. This was confirmed from the time-resolved absorption spectra of the transients formed in the reaction, from the dependence the rate constants on the Marcus energy gap law of electron transfer, and from the lack of correlation of the rate constants with anionic nucleophilicity. In contrast, reactions with unsaturated compounds were observed to proceed via either addition and/or electron transfer depending on the reduction potentials. Electron transfer predominates when the reaction is in the exothermic region, whereas in the endothermic region the reaction followed the alternate pathway, that is, addition reaction.

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