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PHOTOCHEMISTRY OF AQUEOUS AND NON-AQUEOUS SOLUTIONS OF NITRATE

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Nitrate ion undergoes two primary photochemical reactions in aqueous medium depending on the wavelength at which the photolysis reactions are carried out (1). Formation of nitrite ion; and (2) formation by hydroxyl radical. The hydroxyl radical has been trapped by the scavengers like O_2, CNS^- and CO_3^{2-}. To explain the formation of different products, different intermediates, a meta stable and a charge-transfer intermediates have been proposed. In non-aqueous medium, the charge-transfer intermediate and nitrate radical are formed as the primary products. Flash photolysis and steady photolysis methods were used to identify the intermediates and products.

Key Words: Photochemistry; Nitrate; Aqueous and Non-Aqueous Medium

Introduction

The photochemistry of the nitrate ion in aqueous medium has been a subject of number of investigations[1-10]. Nitrate ion undergoes photochemical reactions to yield different products through different pathways under different conditions. It has been the subject of interest to identify the intermediates formed during the course of the photochemical events. The evolution of molecular oxygen and the formation of nitrite ion has been reported and interpreted in terms of a primary act involving a dissociation yielding oxygen atom as

$$*NO_3^- \rightarrow NO_2^- + O \qquad \ldots (1)$$

Daniels *et al.*[6] reported a competitive process for the above when the photochemistry was carried out at 300nm absorption band as

$$*NO_3^- \rightarrow NO_2^- + O^- \qquad \ldots (2)$$

Shuali *et al.*[7] have identified the hydroxyl radical by using scavengers like O_2, CO_3^{2-} and CNS^-. Formation of pernitrite has been reported[5,7,8] on photolysis at 200 nm. Later, Dubovitskii *et al.*[9] proposed a charge-transfer complex between excited and ground state molecules as an intermediate to explain the formation of nitrite and peroxynitrite ions in aqueous medium. Warneck *et al.*[10] explored the photodecomposition product quantum yields at 305nm in aqueous solution and they have used radical trapping technique. Recently[11], the authors have carried out the photochemistry of nitrate ion in acetonitrile and have observed the formation of nitrate radical. In this article these observations are reviewed.

Photochemistry of Nitrate Ion in Aqueous Medium

Nitrate ion shows the absorptions at 200nm with $\varepsilon = 9900\ M^{-}\ cm^{-1}$ which has been attributed to a π-π^* transition and at 300 nm with $\varepsilon = 7.4\ M^{-}\ cm^{-1}$ which has been attributed to n-π^* transition[12-15].

(*a*) *Decomposition of Nitrate Ion*

The formation of nitrite ion and oxygen during photolysis of nitrate ion according to the net reaction

$$NO_3^- \xrightarrow{h\nu} NO_2^- + 1/2\ O_2 \qquad \ldots (3)$$

is rather complicated process and considerable disagreements on the issue exist among many authors. Nitrite ion is formed on photolysis at 200nm as well as at 300nm. Therefore, it has been interpreted as the formation of the product nitrite ion through a common excited state which corresponds to 300nm absorption band.

Shuali *et al.*[7] have studied the nitrite formation at different *p*H values in the 200nm absorption band (Fig. 1). They observed an increase in the yield of nitrite ion above *p*H 5. Both oxygen and nitrite ion are formed in equivalent amounts in the *p*H range $1.8 < pH < 12.8$. Upto the *p*H 11 the general shape agreed with that reported by Daniels[6] on excitation at 300 nm band. Inflection around *p*H 9 in the curve is due to efficient back reaction which takes place at low *p*H range. Above *p*H 10 the rates of evolution of O_2 and the formation of NO_2^- have very little dependence on irradiation interval. Below *p*H 6 a small residual yield is observed for the products NO_2^- and O_2, and is independent of irradiation time. This was initially observed by Daniels[6] in 300 nm photolysis. Daniels proposed that the oxygen atom is responsible for the evolution of molecular oxygen and the sequence are

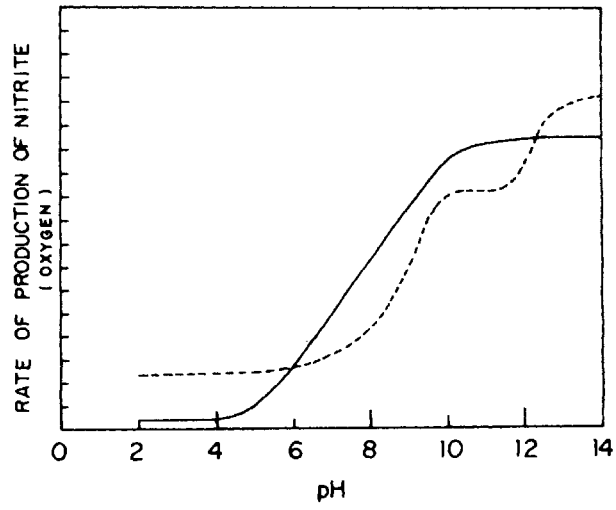


Fig 1 Dependence of nitrite yield on *p*H. Solid curve (after Shuali *et al.*[7]) dashed curve (after Daniels *et al.*[6])

$$^*NO_3^- \rightarrow NO_2^- + O \quad \ldots (1)$$

$$\text{and } O + NO_3^- \rightarrow NO_2^- + O_2. \quad \ldots (4)$$

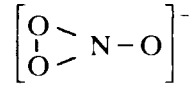
They also proposed another reaction responsible for the residual yield at low *p*H which is

$$O + NO_2^- \rightarrow NO_3^- \quad \ldots (5)$$

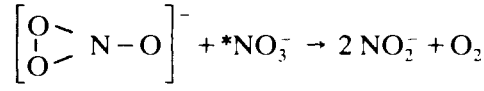
This was supported by their experimental evidence that the amount of nitrite ion does not increase even in the presence of externally added NO_2^- ion and furthermore there is a consumption of nitrite ion.

But Shuali *et al.*[7] contradicted this proposal for the oxygen atom as the intermediate based on their observation, in the presence of other solutes which also compete for the atomic oxygen with NO_3^-, that there is a decrease in the amounts of formation of O_2 and NO_2^-. They have excluded the $O(^1D)$ because no measurable amount of H_2O_2 was observed[16]. Since oxygen does not influence the yield of nitrite ion, they have ruled out the possibility of $O(^3P)$ becoming the intermediate. Formation of O_3 is reported[17] by the reaction of $O(^3P)$ with O_2 which should compete with NO_3^- if $O(^3P)$ would have been the intermediate.

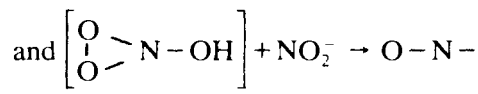
Based on these arguments, Shuali *et al.*[7] proposed a meta stable intermediate



as the oxygen evolving intermediate. The sharp drop in the yields of O_2 and NO_2^-, as the decrease in *p*H, was explained by the acid and base forms of the intermediate as



$$\ldots (6)$$



$$\ldots (7)$$

Dubovitskii *et al.*[9] interpreted the dependence of yield of nitrite ion *p*H in a different manner. Nitrate ion is a good electron acceptor and, indeed, excited state NO_3^- is a better electron acceptor than ground state NO_3^-. During collision of these ions in solution, a doubly charged NO_3^{2-} anion and NO_3 radical complex results.

$$^*NO_3^- + NO_3^- \rightarrow [NO_3^{2-} + NO_3] \quad \ldots (8)$$

NO_3^{2-} anion decomposes[18] rapidly in aqueous solution with the formation of NO_2 and OH^-.

The presence of NO_3 radical leads to the formation of nitrous anhydride.

$$NO_2 + NO_3 \rightarrow N_2O_3 + O_2. \quad (9)$$

Further, N_2O_3 enters into an irreversible reaction with OH^- ions.

$$N_2O_3 + 2\,OH^- \rightarrow 2\,NO_2^- + H_2O. \quad \ldots (10)$$

Thus, the collision complex is also able to explain the formation of nitrite and molecular oxygen in aqueous medium.

The reaction leading to the formation of NO_2^- is characteristic of alkaline solutions, when the NO_3^{2-} anion is not protonated. The rate as well as the quantum yield of formation of NO_2^- is dependent on the concentration of OH^- ions and therefore a decrease in *p*H of the solution will reduce the quantum yield of nitrite ion formation.

In neutral and acid solutions, the NO_3^{2-} is protonated[15]

$$NO_3^{2-} + H^+ \rightleftharpoons HNO_3^- \overset{H^+}{\rightleftharpoons} H_2NO_3 \qquad \ldots (11)$$

and the *p*H values are 7.5 and 4.8 respectively. The HNO_3^- acid decomposes into NO_2 and OH^- ($t_{1/2} = 3\mu$ sec). Thus at *p*H values less than 7.5, the separation of the radical pair will occur mainly by protonation of NO_3^{2-} anion. In this case the formation of NO_2^- as photolysis product will be related to the reaction (9) and to subsequent reaction of nitrous anhydride with water.

$$N_2O_3 + H_2O \rightarrow 2H^+ + 2NO_2^- \qquad \ldots (12)$$

This explains the decrease of the initial rate of accumulation of NO_2^- in neutral and acid solutions (Fig. 2).

Daniels claim that peroxynitric acid, $HOONO_2$ with *p*K of about 8, is responsible for the apparent titration curve as shown in Fig. 1. This has been shown improbable by Wagner *et al.*[8] and they have proposed the following alternatives. The major deactivations of $^*NO_3^-$ are by the following reactions.

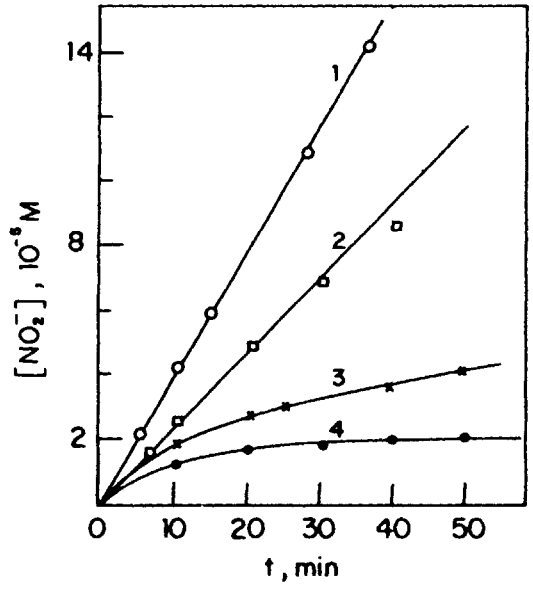


Fig 2 Dependence of nitrite yield with time at *p*H (1) 12.4; (2) 9.3; (3) 6.8; (4) 2.4 on irradiation of 1M aqueous solution of $NaNO_3$ (after Dubovitskii *et al.*[9]).

Table I

pk values of peroxynitrous acid

pk	Reference
5.3	Gratzel *et al.*[18]
6.3	Shuali *et al.*[8]
< 6.0	Yagil and Anbar[20]
8.3	Hughes and Nicklin[21]
6.0	Barat *et al.*[22]
6.6	Keith and Powell[23]

Table II

Rate constants of the relevant reactions

Reaction	Rate constant	Reference
$OH + NO_2^- \rightarrow OH^- + NO_2$	$10^{10}\ M^{-1}s^{-1}$	12, 26
$O^- + O_2 \rightarrow O_3^-$	$2.5 \times 10^9\ M^{-1}s^{-1}$	26
$O + O_2 \rightarrow O_3$	$\sim 5.0 \times 10^9\ M^{-1}s^{-1}$	17
$O + NO_2^- \rightarrow NO_3^-$	$\sim 2.0 \times 10^9\ M^{-1}s^{-1}$	17
$O + NO_3^- \rightarrow O_2 + NO_2^-$	$\sim 3.0 \times 10^8\ M^{-1}s^{-1}$	17
$OH + NO_2 \rightarrow HOONO$	$1.2 \times 10^{10}\ M^{-1}s^{-1}$	8
	$1.3 \times 10^9\ M^{-1}s^{-1}$	18
$OONO_2^- \rightarrow NO_3^- + O$	$0.015\ s^{-1}$	8
$OONO_2^- + NO_3^- \rightarrow NO_3^- + NO_2^- + O_2$	$25\ M^{-1}s^{-1}$	8
$N_2O_3 + H_2O \rightarrow 2\,HNO_2$	$530\ s^{-1}$	21
$[NO_3^- \text{---} NO_3] \rightarrow 2\,NO_2^- + O_2$	$35\ s^{-1}$	11
$NO_3 + CH_3CN \rightarrow HNO_3 + CH_2CN$	$21\ s^{-1}$	11

$H^+ + {}^*NO_3^-\ (300\ nm) \rightarrow OH + NO_2$ ... (13)

and ${}^*NO_3^- \rightarrow NO_2^- + O$ ... (1)

At any *p*H the primary products of ${}^*NO_3^-$ (300 nm) are either

${}^*NO_3^-\ (300\ nm) \rightarrow O^- + NO_2^- + O$ ... (13')

or ${}^*NO_3^-(300\ nm) \rightarrow NO_2^- + O$ ... (1)

together with reaction (4)

$O + NO_3^- \rightarrow NO_2^- + O_2$ ... (4)

both being independent of *p*H , are responsible for the residual yield of NO_2^- obtained at low *p*H .

The following subsequent reactions are considered to explain the titration curve.

$$O^- + H^+ \rightarrow OH \quad \ldots (14)$$

$$O^- + H_2O \rightarrow OH + OH^- \quad \ldots (15)$$

$$O^- + NO_2^- + H_2O + \rightarrow NO_2 + 2OH^- \quad \ldots (16)$$

$$O^- + NO_2 \rightarrow O + NO_2^- \quad \ldots (17)$$

$$O^- + NO_2 \rightarrow NO_3^- \quad \ldots (18)$$

$$2\,O^- \rightarrow O_2^{2-} \rightarrow H_2O_2 + 2\,OH^- \quad \ldots (19)$$

$$\text{and } O^- + NO_2 \rightarrow OONO^-. \quad \ldots (20)$$

Of these reactions, reactions (16) and (19) are slower and cannot compete with other reactions because of electrostatic repulsion. The OH radical is deactivated by the following reactions

$$OH + NO_2^- \rightarrow OH^- + NO_2 \quad \ldots (21)$$

$$\text{and } 2\,OH \rightarrow H_2O_2. \quad \ldots (22)$$

Reaction (20) may be neglected since no peroxynitrite is detected with 300nm excitation although peroxynitrite is stable under these conditions. The OH radical produced react efficiently with nitrite ion and thus leading to the self inhibition of nitrite production. Under residual yield conditions these reactions (20) and (21) do not contribute to the nitrite production.

The rate constant k_1 and k_{13} can be written as

$$k_1 = k'_1 + k'_{13}\frac{k_{17}[NO_2]}{k_{14}[H^+] + k_{15} + (k_{17} + k_{18})[NO_2]} \quad \ldots (23)$$

$$\text{and } k_{13} = k'_{13}\frac{k_{14}[H^+] + k_{15}}{k_{14}[H^+] + k_{15} + (k_{17} + k_{18})[NO_2]} \quad \ldots (24)$$

At low pH $k_{14}[H^+]$ is much larger than the other terms in the denominator of equations 23 and 24. Then $k_1 \simeq k_1$ and $k_{13} \simeq k'_{13}$. At higher pH above 5, $k_{14}[H^+]$ is much reduced and therefore may be neglected. As a result k_1 is remarkably increased causing increased production of nitrite ion.

The increase in the yield of nitrite ion is explained by the pK = 12 of OH radical. In strongly alkaline solutions the reaction 15 does not shift to the right hand side and hence does not contribute in the equations. This results in the second step in the yield-pH curve (Fig. 1). Otherwise the qualitative difference is due to the different experimental conditions under which the experiments were carried out by Daniels *et al.*[6] and Shuali *et al.*[7].

Warneck *et al.*[10] reported the quantum yield of O-atom and OH radical in aqueous medium at 305nm as $\phi_{(O)} = 1.1$ E-03 and $\phi_{(OH)} = 9.2$ E-03 using cyclopentene and 2-propanol as the scavengers respectively. It has been considered that nitrite is formed on photolysis directly (1) in the primary event

$$^*NO_3^- \rightarrow NO_2^- + O \quad \ldots (1)$$

and in the secondary event (4)

$$O + NO_3 \rightarrow O_2 + NO_2^- \quad \ldots (4)$$

and also the NO_2^- ion is consumed by the reaction

$$O_3 + NO_2^- \rightarrow O_2 + NO_3^-. \quad \ldots (25)$$

O_3 is obtained by the reaction of O-atom with the oxygen molecule

$$O + O_2 \rightarrow O_3. \quad \ldots (26)$$

(b) Formation and Isomerisation of Peroxynitrite Ion

Formation of peroxynitrite on photolysis at high energy band has been observed by Daniels *et al.*[6] and Shulai *et al.*[7]. On flash photolysis[7] of nitrate ion in aqueous medium in the range of $5 < p\text{H} < 8$, a stable peak at 300nm and a transient absorption at 245nm have been observed. An isosbestic point around 265nm has been observed when the spectra were recorded in the range $5 < p\text{H} < 8$. Below $p\text{H} = 5$ the stable peak at 300nm is replaced by transient, characterised by a tailing absorption at 245nm.

Fig. 3 represents the changes in absorbance at 245 and 290nm with *p*H. From the symmetry of the titration curve the assignment of 290 and 245nm absorptions

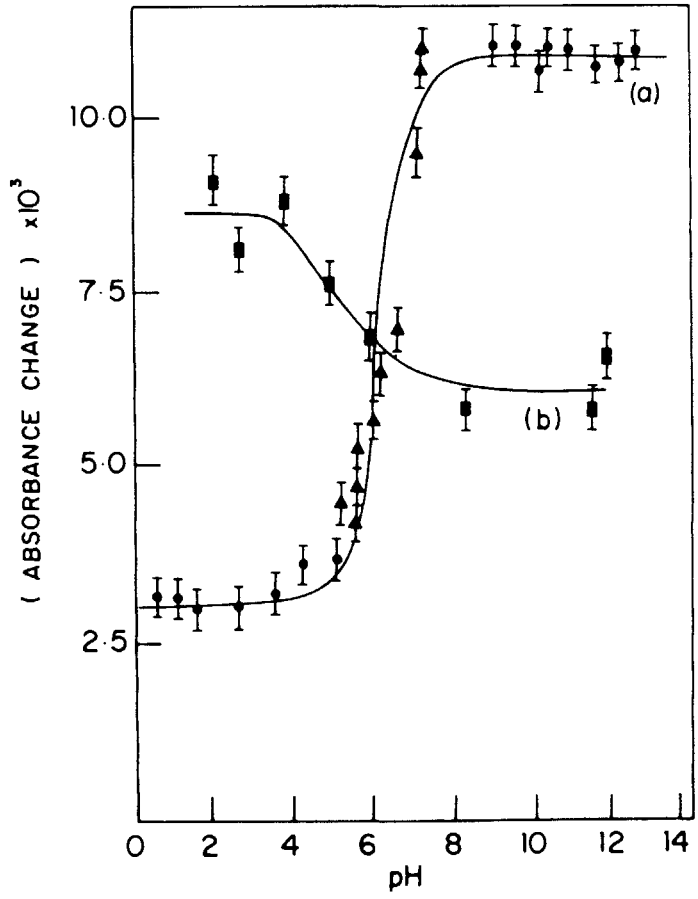


Fig 3 *p*H dependence of absorbance changes measured 1ms after photolysis of an argon saturated solution 5×10^{-3} M KNO_3 (*a*) ●, ▲ absorbance change at 290nm; (*b*) ■ absorbance change at 245nm. The *p*H was regulated with NaOH or $HClO_4$ (●, ■) or phosphate buffer (▲) (after Shuali *et al.*[7])

to the peroxynitrite ion and peroxynitric acid have been confirmed. The sharp inflection between *p*H 5 and 7 is due to the equilibrium

$$H^+ + OONO^- \rightleftharpoons HOONO \quad \ldots (27)$$

with *p*K value of 6.

Peroxynitrous acid formed on photolysis of 200nm band is not stable but isomerises to nitric acid.

$$HOONO \rightarrow H^+ + NO_3^- \quad \ldots (28)$$

The rate constant of the isomerisation reaction is given by

$$k_{28}^{obs} = k_{28}(1 + K_{27}/[H^+])^{-1}, \quad \ldots (29)$$

where K_{27} is the dissociation constant of peroxynitrous acid. The isomerisation reaction has been studied by Benton and Moore[19] using stopped-flow method and at low *p*H acid catalysis has been observed for the isomerisation reaction.

$$k_{28} = k_{28}^0 + k_{28}^H[H^+]. \quad \ldots (30)$$

For the whole range of *p*H

$$k_{28}^{obs} = \frac{k_{28}^0 + k_{28}^H[H^+]}{1 + K_{27}/[H^+]} \quad \ldots (31)$$

The rate constants for these reactions have been obtained by Wagner *et al.*[8] and are $k_{28}^0 = 1.22 \pm 0.01\ s^{-1}$ and $k_{26}^H = 17 \pm 4\ M^{-1}\ s^{-1}$. The *p*K values obtained by different authors are tabulated in Table 1.

(*c*) *Formation of Peroxynitric Acid*

The formation and the decay of an oxidising species has been reported by Wagner *et al.*[10] with the lifetime of about 40s using conductance detection technique. They have identified it as peroxynitric acid and they have excluded the possibility of this oxidising species becoming H_2O_2, O_2 and O_3 by making the following observations:

(1) The amplitude of the trace increased with the addition hydrogen peroxide.
(2) The rate does not depend on the concentration of nitrite but enhanced by the addition of nitrate ion.
(3) Iodine is liberated when KI is added, 10 seconds after photolysis.

They have ruled out O_2 and H_2O_2 since the reactions between HNO_2 and H_2O_2, and O_2 are slower. O_3 is excluded because the reaction between O_3 and HNO_2 has a half-life of 0.15s. Peroxynitric acid is formed by the following reactions:

$$2\,OH \rightarrow H_2O_2, \quad \ldots (22)$$

$$H_2O_2 + OH \rightarrow H_2 + HO_2; \quad \ldots (32)$$

$$\text{and } HO_2 + NO_2 \rightarrow HOONO_2 \quad \ldots (33)$$

and the peroxynitric acid decays by the following reactions:

$$OONO_2^- \rightarrow NO_3^- + O \quad \ldots (34)$$

$$O + NO_3^- \rightarrow NO_2^- + O_2 \quad \ldots (4)$$

$$O + NO_2^- \rightarrow NO_3^- + \quad \ldots (5)$$

Photochemistry of Nitrate Ion in Acetonitrile

The author has recently explored[11] the photochemistry of nitrate ion by taking the cobalt(II) nitrate as the substrate, and by performing steady-state and flash photolysis experiments.

Steady photolysis of cobalt(II) nitrate in both air-equilibrated and argon saturated acetonitrile result a new absorption band around 355nm and a shoulder around 290nm. These are similar to the n-π^* transition of nitrate anion[24]. So it is inferred that nitrite ion is formed as a product during photolysis. It has also been observed that cobalt(II) concentration does not change on photolysis.

Flash photolysis of cobalt(II) nitrate ion in air-equilibrated acetonitrile results transient absorption over the region 350 to 700nm in 200ms time scale with the maxima around 400 and 675nm. The transient absorption at 400nm obeys first order kinetics and the rate constant is 35 s^{-1}. The transient absorption at 700nm also obeys first order kinetics with the rate constant of 21 s^{-1}. In argon saturated medium the transient absorptions around 600nm were not observed but only 400nm transient absorption is observed (Fig. 4).

The absorptions at 620 and 675nm are characteristic of nitrate radical[25,26]. It is inferred that nitrate radical is formed on direct photolysis of nitrate ion and which has not been observed in argon saturated medium due to the recombination of the electron and nitrate radical. In air-equilibrated medium, oxygen available in the medium acts as a good scavenger for solvated electron.

The transient absorption at 400nm in both air-equilibrated and argon saturated medium is assigned to the formation of electron transfer complex [NO_3^{2-} --- NO_3] obtained by the reaction between the excited and the ground state NO_3^- ions and result in the production of NO_2^- and oxygen. The experimental evidence for the above complex is that the 400nm transient absorption is not seen in the presence of 2M ethanol, where ethanol reacts with nitrate radical and gets oxidised and also transient absorption obeys only first-order kinetics.

The observations made by us are explained by following sequences. The excited state of nitrate ion is deactivated by two modes, one through the formation of nitrate radical and the other through the collision electron transfer complex:

$$^*NO_3^- \rightarrow NO_3^- + e_{sol} \quad \ldots (35)$$

$$NO_3^- + CH_3CN \rightarrow HNO_3^- + CH_2CN \quad \ldots (36)$$

$$^*NO_3^- + NO_3^- \rightarrow [NO_3^{2-} \text{---} NO_3] \quad \ldots (8)$$

$$[NO_3^{2-} \text{---} NO_3] \rightarrow 2\,NO_2^- + O_2 \quad \ldots (37)$$

Conclusion

In aqueous medium excited state of nitrate ion is deactivated to generate NO_2 and O^-, NO_2 and oxygen, and peroxynitrite and peroxynitrate species. In non-aqueous medium, the excited state of nitrate ion is deactivated through collision electron ransfer complex, which has been observed in aqueous medium also, to form nitrite ion and molecular oxygen and also through the nitrate radical.

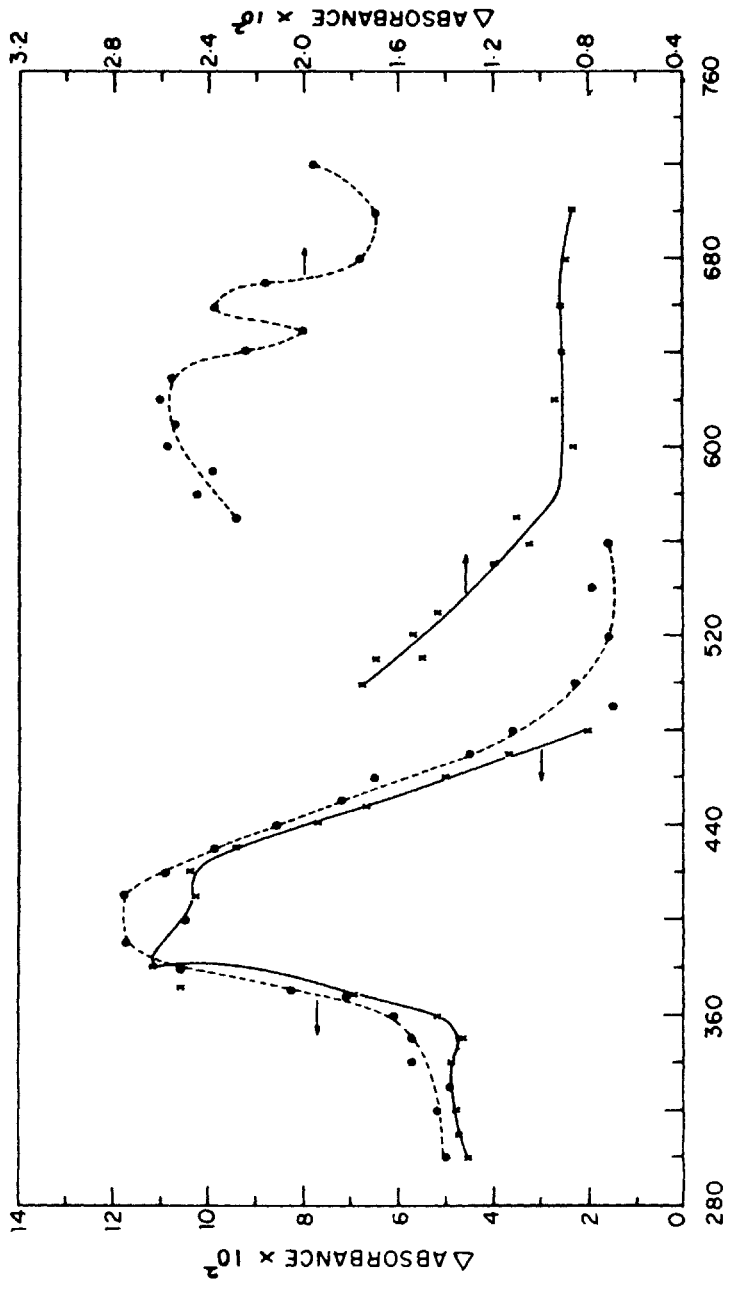


Fig 4 Transient absorption spectrum recorded at 10 ms after flash. (●) In air-equilibrated acetonitrile; (×) in argon-saturated acetonitrile.

Acknowledgement

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