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THE REACTIVITY OF THE ELECTRON FORMED IN THE RADIOLYSIS OF AERATED ALKALINE AQUEOUS SOLUTIONS CONTAINING TETRACYCLINE HYDROCHLORIDE, AT 77 K[+]

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The present study deals with the radiolysis of tetracycline hydrochloride dissolved in aerated alkaline aqueous solutions containing 0.1, 0.5 and 1M NaOH, at 77 K, as followed by ESR. The rate constants for the reactions between the electron and physical and chemical traps which are present in these solutions are calculated. These values are $k_{ph} = 9.6 \cdot 10^{15}\ l \cdot mol^{-1} \cdot s^{-1}$ and $k_{ch} = 1.3 \cdot 10^{10}\ l \cdot mol^{-1} \cdot s^{-1}$. The reactivity of electrons that are formed in the radiolysis of water decreases in the following proportions: physical traps: chemical traps: molecules of water: $4.8 \cdot 10^{14} : 6.5 \cdot 10^{8} : 1.0$. The electrons react preferentially with the solute instead of the solvent.

Introduction

The interaction of gamma radiation with matter produces electrons, which can be observed by ESR at low temperature when chemical traps[1–3] such as tetracycline hydrochloride (TC)[4] or physical traps[5–8] as Na^+ ions, are present. In 1977 DZIEGIELWESKI determined the rate constant for the reaction between the electron and TC, k_{ch}, in the radiolysis of methanolic and aqueous solutions.[4] But the determination of the rate constant for the reaction between the electron and a physical trap, k_{ph}, requires knowledge of the concentration of physical trap.

It is possible to determine only the relation (k_{ch}/k_{ph} [physical trap])[1] from the competitive reactions between the electron and these traps. In 1982 RAITSIMRING and co-workers[9] calculated the concentration of the physical traps for 4M to 9M XOH solutions (X represents Na, Li or K). Therefore, it was possible in the present work to obtain the values of k_{ph} and k_{ch} in the radiolysis of 0.1, 0.5 and 1M NaOH containing TC, at 77 K. The electron formed in the radiolysis of water, at 77 K, reacts preferentially with the traps instead of the solvent.

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Experimental

The water used was deionized by ion exchange and distilled in a quartz distiller. The TC and NaOH used were of analytical grade. Three series of samples were prepared in the presence of air with the following concentrations of NaOH: 0.1, 0.5 and 1M. Each series of 14 samples ($0 \leqslant [TC] \leqslant 0.052M$) was prepared the same day and in the following day these samples were irradiated simultaneously, at 77K, and the ESR spectra were recorded on a JEOL JES–ME–3 spectrometer, at 77 K, after the irradiation. The three series were irradiated with the same dose of 3 kGy in a ^{60}Co-gamma cell 220 source from Atomic Energy of Canada Limited.

Results and discussion

In the radiolysis of water, at 77 K, H· and a radical corresponding to an impurity were formed besides OH· and $HO_2\cdot$[10] (Fig. 1). When the radiolysis of water, at 77 K, occurs in the absence of air, it is observed that the impurity comes from the air (Fig. 1b).

In the radiolysis of alkaline solutions, at 77 K, the air does not interfere in the formation of radicals observed by ESR (Table 1). In these solutions the electrons are observed by ESR, because physical traps are present[11,12] (Fig. 2a–c). When TC is added to these solutions the electrons are also captured by chemical traps[4,13] (Fig. 2d–f).

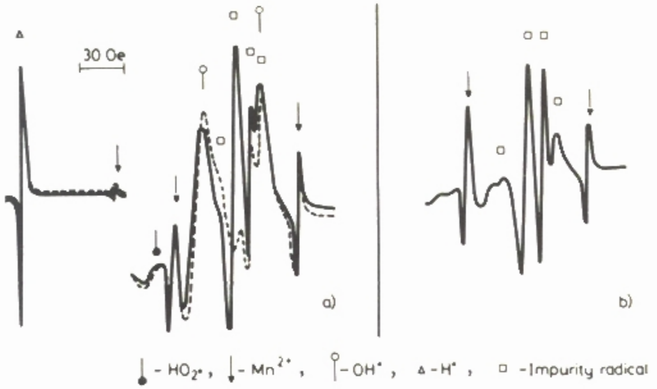


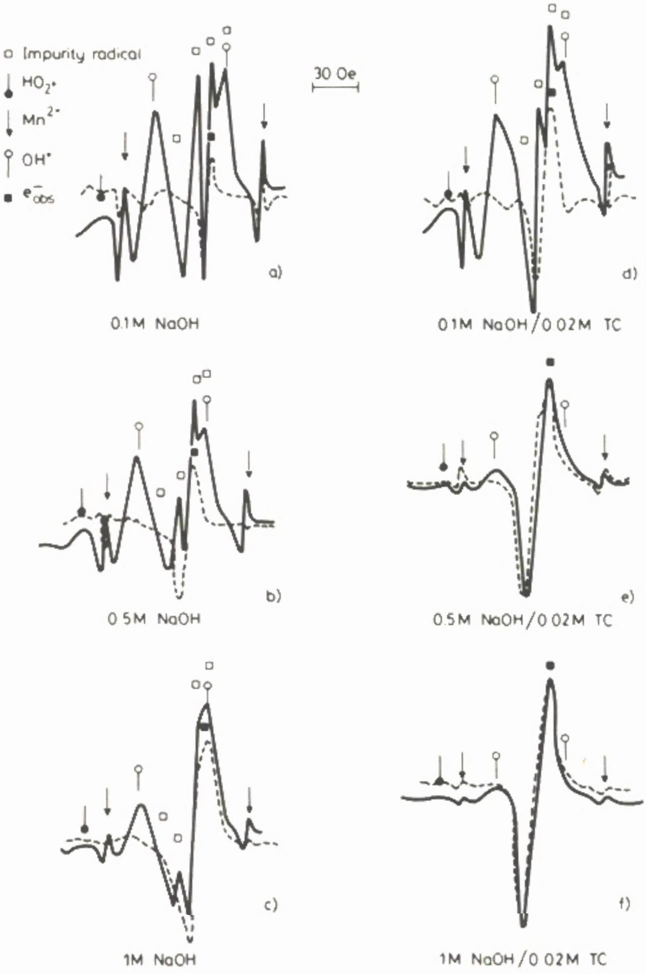
Fig. 1. Radiolysis of water at 77 K; (a) —— in the presence of air, - - - - without air, (b) the impurity radical was obtained by subtracting the ESR spectrum of water from Reference 10 from the ESR spectrum of water of (a)

Fig. 2. Radiolysis of alkaline aerated aqueous solutions containing TC, at 77 K; —— ESR spectra of alkaline solution, - - - - ESR spectra obtained by subtraction between alkaline solution and water spectra (a–d) or spectrum of TC in powder form (e, f). Reference 17 presents the spectrum of TC in powder form

Table 1

Influence of air on the relative yield of paramagnetic species formed in the radiolysis of alkaline aerated aqueous solutions containing TC, at 77 K

Sample	Air	$RY_{(H\cdot)}$	$RY_{(OH\cdot)}$	$RY_{(HO_2\cdot)}$	$RY_{(e^-_{obs})}$
1M NaOH/TC(0.04M)	Absent	29.2	1.1	0.2	25.1
1M NaOH/TC(0.04M)	Present	28.4	0.8	0.2	21.2
$RY_{(abs.)}/RY_{(pres.)}$	–	1.0	1.4	1.0	1.2
0.5M NaOH/TC(0.04M)	Absent	20.2	1.4	0.2	13.6
0.5M NaOH/TC(0.04M)	Present	25.9	1.3	0.2	13.2
$RY_{(abs.)}/RY_{(pres.)}$	–	0.8	1.1	1.0	1.0



The values of the rate constants for these reactions can be obtained considering that Reaction (1), where the electron is trapped by Na^+ ion, competes with Reaction (2), where the electron is captured by TC:

$$e^- + T \xrightarrow{k_{ph}} e_t^- , \qquad (1)$$

$$e^- + TC \xrightarrow{k_{ch}} e_c^- \qquad (2)$$

where T represents one physical trap formed by the solvated Na^+ ion;

e_t^- and e_c^- represent the electron trapped by a physical trap and captured by a chemical trap, respectively;

k_{ph} and k_{ch} are the rate constants of the Reactions (1) and (2), respectively. Then

$$\frac{RY_{(e^-_{obs})}}{RY_{(e^-_t)}} = 1 + \frac{k_{ch}[TC]}{k_{ph}[T]} \qquad (3)$$

Where RY represents the relative yield of species and $RY_{(e^-_{obs})} = RY_{(e^-_t)} + RY_{(e^-_c)}$.

In Fig. 3 the $(RY_{(e^-_{obs})} / RY_{(e^-_t)})$ is plotted versus [TC] for three series of 0.1, 0.5 and 1M NaOH solutions and it can be observed that the intercept corresponding to Eq. (3) is equal to 1 for the 0.1M NaOH series, while for the other two series the intercepts are 1.27 and the slopes are larger, indicating that TC is more efficient for the capture of electrons when it is dissolved in concentrated NaOH solutions. This fact is associated with degradation reactions of TC,[14–17] because compounds are formed that are more efficient for electron capture than TC.[18–20]

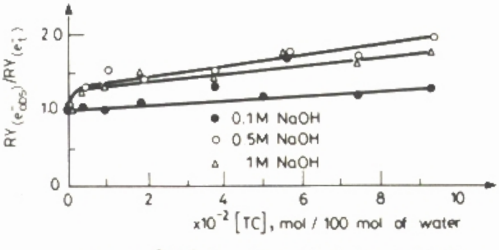


Fig. 3. $(RY_{(e^-_{obs})} / RY_{(e^-_t)})$ against [TC] for the radiolysis of alkaline aerated solutions at 77 K. $(k_{ch}/k_{ph}[TC])$ is 2.68; 6.57; 5.03 for 0.1, 0.5 and 1M NaOH solution, respectively

Therefore, the 0.1M NaOH solution can be considered a dilute solution, because the alkali degradation does not affect this efficiency for TC and $(k_{ch})_{0.1M} = 1.46 \cdot 10^9$ $l \cdot mol^{-1} \cdot s^{-1}$.[4]

The value of k_{ph} of Eq. (3) can be obtained if one knows $[T]_{0.1M}$. RAITSIMRING and co-workers[9] calculated [T] in 4 to 9M XOH (X represents Na, Li or K) considering the formation of the geminated ionic pair (e^-/H_2O^+), where e^- recombines with H_2O^+ ion in the presence of physical traps. They also observed another paramagnetic species, O^-. This species was also observed by TROUNG[3] and it is formed in the same concentration as e_t^-. This species is expected to form in concentrated alkali solution and decreases the $RY_{(OH\cdot)}$ $(OH^- + OH\cdot \longrightarrow O^- + H_2O)$.

In order to obtain [T] for 0.1, 0.5 and 1M NaOH solutions from the values obtained by RAITSIMRING and co-workers,[9] a sample of 4M NaOH was irradiated, in the presence of air, at 77 K, and the experimental values (Table 2) show that the species O^- does not form in solutions where $[NaOH] \leqslant 1M$, but it forms in solutions where $[NaOH] \geqslant 4M$. Therefore, $RY_{(e^-_{obs})} = RY_{(e^-_t)} + RY_{(e^-_c)}$ in solutions where $[NaOH] < 1M$ and $0 \leqslant [TC] \geqslant 0.052M$.

The values of [T] obtained from the experiments performed by RAITSIMRING and co-workers[9] and the values of the rate constants for the reactions between the electron and physical and chemical traps are shown in Table 3. The average of k_{ch} equals 1.3×10^{10} $l\,mol^{-1}\ s^{-1}$. The electrons are trapped specifically by Na^+ ions, though the efficiency of electron capture by TC increases about 10 times because the TC is degraded in alkaline solutions. The Na^+ ions are $7.4 \cdot 10^5$ times more efficient in trapping the electron than TC, in $0.1M \leqslant [NaOH] \leqslant 1M$ aerated aqueous solutions.

Table 2

Values of $\%(e^-_{obs})$ and of $RY_{(OH\cdot)}$ in the radiolysis of alkaline solutions ($[NaOH] \leqslant 4M$) in the presence of air at 77 K

	NaOH concentration			
	0.1M	0.5M	1M	4M
$\%(e^-_{obs})$	12.8	36.2	47.3	84.3
$RY_{(OH\cdot)}$	1.4	1.4	1.4	0.61

Table 3

Rate constants for the reactions between the electron and physical and chemical traps

Kind of trap	[NaOH], M	$[T], l^{-1}$	$k, (l \cdot mol^{-1} \cdot s^{-1})$
Physical	$\leqslant 1$	$\leqslant 1.5 \cdot 10^{17}$	$9.6 \cdot 10^{15}$
Chemical	1	$1.5 \cdot 10^{17}$	$2.2 \cdot 10^{10}$
Chemical	0.5	$7.9 \cdot 10^{16}$	$1.5 \cdot 10^{10}$
Chemical	0.1	$1.9 \cdot 10^{16}$	$1.5 \cdot 10^{9}$

Table 4
Radiolysis of aqueous solutions, at 77 K: rate constants for reactions between electrons and species present

Reaction	Reactions of electrons*	K, $l \cdot mol^{-1} \cdot s^{-1}$	Reference
1	$e^- + H_2O \longrightarrow H\cdot + OH^-$	$2.0 \cdot 10^{1}$	21
2	$e^- + TC^+ \longrightarrow TC$	$1.5 \cdot 10^{9}$	4
3	$e^- + TC \xrightarrow[0.1M\ NaOH]{} e^-_c$	$1.5 \cdot 10^{9}$	**
4	$e^- + e^- \xrightarrow[H_2O]{} H_2 + OH^- + OH^-$	$5.0 \cdot 10^{9}$	21
5	$e^- + NO_3^- \longrightarrow NO_3^{2-}$	$8.5 \cdot 10^{9}$	1
6	$e^- + H_2O_2 \longrightarrow OH\cdot + OH^-$	$1.2 \cdot 10^{10}$	21
7	$e^- + NpO_2(CO_3)_3^{4-} \xrightarrow[(CO_3)^{2-}]{} NpO_2(CO_3)_3^{5-}$	$1.3 \cdot 10^{10}$	1
8	$e^- + TC \xrightarrow[0.5M\ NaOH]{} e^-_c$	$1.5 \cdot 10^{10}$	**
9	$e^- + O_2 \longrightarrow O_2^-$	$1.9 \cdot 10^{10}$	1,21
10	$e^- + H^+ \longrightarrow H\cdot$	$2.2 \cdot 10^{10}$	1,21
11	$e^- + TC \xrightarrow[1M\ NaOH]{} e^-_c$	$2.2 \cdot 10^{10}$	**
12	$e^- + H\cdot \xrightarrow[H_2O]{} H_2 + OH^-$	$2.5 \cdot 10^{10}$	21
13	$e^- + OH\cdot \longrightarrow OH^-$	$3.0 \cdot 10^{10}$	21
14	$e^- + T \xrightarrow[\leqslant 1M\ NaOH]{} e^-_t$	$9.6 \cdot 10^{15}$	**

*In Reactions (1) to (13) the chemical species that react with the electron are considered as chemical traps and in reaction 14, T is considered as physical trap.

**The value of K was obtained in this work.

Table 5
Reactivity of electrons formed in the radiolysis of NaOH/TC aerated aqueous solutions at 77 K

Reactivity of electron	with	in relation to
$4.8 \cdot 10^{14}$	Physical traps	Solvent
$6.5 \cdot 10^{8}$	Chemical traps	Solvent
$7.4 \cdot 10^{5}$	Physical traps	Chemical traps

It is interesting to note in Table 4 that the rate constants (reactions 2 to 13) vary from 10^9 to 10^{10} $l \cdot mol^{-1} \cdot s^{-1}$ and are independent of the kind of chemical trap (molecules, cations or anions). Therefore, the reactivity of the electron formed in the radiolysis of water is also independent of the kind of chemical species that behave as chemical traps.

Table 5 shows the order of reactivity of the electron formed in the radiolysis of water with physical and chemical traps with regard to solvent. The electrons react especially with solutes, though the proportion between solutes and solvent varied from 1:53 to 1:556.

MIYAZAKI and co-workers[22–24] ascribed the occurrence of the selective reaction of abstraction of the solute hydrogen atom by a hydrogen atom produced during radiolysis of the solvent to channels formed by the solvent molecules at 77 K. The hydrogen atom can migrate through the channels formed by solvent molecules and react with the solute molecule.[25–27]

The values of the rate constants for the reactions between electron and solutes may indicate that electron shows a behaviour similar to H·, when they are formed in the radiolysis of alkaline aerated solutions, at 77 K.

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References

1. A. K. PIKAEV, B. G. ERSHOV, I. E. MAKAROV, J. Phys. Chem., 79 (1975) 3025.
2. C. STRADOWSKI, Bull. Acad. Pol. Sci. Sér. Sci. Chim., 27 (1979) 919.
3. T. B. TRUONG, J. Phys. Chem., 67 (1977) 1957.
4. J. D. DZIEGIELEWSKI, Bull. Acad. Pol. Sci. Sér. Sci. Chim., 25 (1977) 131.
5. M. J. BLADAMER, L. SHIELDS, M. C. R. SYMONS, J. Chem. Soc., (1964) 4352.
6. L. KEVAN, J. Am. Chem. Soc., 87 (1965) 1481.
7. J. MOAN, Proc. Cong. Radiation Research, Washington 14–20 July, 1974, O. F. NYGAARD, H. I. ADLER, W. K. SINCLAIR (Eds), 1975, p. 450.
8. L. KEVAN, Proc. Cong. Radiation Research, Washington 14–20 July, 1974, O. F. NYGAARD, H. I. ADLER, W. K. SINCLAIR (Eds), 1975, p. 406.
9. A. M. RAITSIMRING, L. A. RAPATSKII, R. I. SAMOILOVA, Yu. D. TSEVETKOK, High Energy Chem., 16 (1982) 232.
10. B. H. J. BIELSKI, J. M. GEBICKI, Atlas of Electron Spin Resonance Spectra, Academic Press, New York, 1967. p. 643.
11. P. POLEVOI, A. PLONKA, Radiochem. Radioanal. Letters, 36 (1978) 235.
12. T. HENRIKSEN, Radiat Res., 23 (1964) 63.
13. M. C. R. SYMONS, Pure Appl. Chem., 53 (1981) 223.
14. E. LAGERCRANTZ, M. YHLAND, Acta. Chem. Scand., 17 (1963) 2568.
15. C. R. STEPHENS, L. H. CONOVER, F. A. HOCHSTEIN, P. R. REGNA, F. J. PILGRIM, K. J. *BRUNINGS, R. B. WOODWARD, J. Am. Chem. Soc., 74 (1952) 4975.*
16. C. W. WALLER, B. L. HUTCHINGS, A. A. GOLDMAN, C. F. WOLF, R. W. BROSCHARD, J. H. WILLIAMS, J. Am. Chem. Soc., 74 (1952) 4979.

17. S. M. L. GUEDES, Study of the radiolysis of tetracycline hydrochloride in powder form, in aqueous solutions and in benzyl alcohol at 77 K, by ESR, Doctoral thesis, IPEN–CNEN/SP, August 1984.
18. D. L. J. CLIVE, Q. Rev., 22 (1968) 435.
19. R. G. KELLY, H. A. FLOYD, K. D. HOYT, Proc. Conf. Antimicrobial Agents Chemoterapy, Philadelphia, 26–28 October, 1966, G. L. HOBBY (Ed.), 1966, p. 666.
20. B. VEJ-HANSEN, H. BUNDGARD, Arch. Pharm. Chem. Sci., 6 (1978)201.
21. A. W. BOYD, M. B. CARVER, R. S. DIXON, Radiat. Phys. Chem., 15 (1980) 177.
22. T. MIYAZAKI, T. HIRAYAMA, J. Phys. Chem., 79 (1975) 566.
23. T. MIYAZAKI, S. M. L. GUEDES, L. G. ANDRADE E SILVA, L. FERNANDES, Bull. Chem. Soc. Japan, 50 (1977) 301.
24. T. MIYAZAKI, J. KASUGAI, M. NADA, K. KINUGAWA, Bull. Chem. Soc. Japan, 51 (1978) 1976.
25. T. MIYAZAKI, K. KINUGAWA, M. EGUCHI, S. M. L. GUEDES, Bull. Chem. Soc. Japan, 49 (1976) 2970.
26. T. MIYAZAKI, Bull. Chem. Soc. Japan, 50 (1977) 1625.
27. K. KINUGAWA, T. MIYAZAKI, H. HASE, Radiat. Phys. Chem., 10 (1977) 341.