PHOTOLYSIS OF SODIUM CYANIDE IN AQUEOUS SOLUTION

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(Received December 12, 1979)

Summary

The initial quantum yields Q_i obtained by indirect photolysis of dilute aqueous alkaline solutions of CN^- ions at 184.9 nm are $Q_i(NH_3) = 0.27$, $Q_i(HCHO) = 0.07$, $Q_i(HCOO^-) = 0.10$ and $Q_i(-CN^-) = 0.29$. Although CO_2 was also formed, its quantum yield was not determined. Based on these results, and by means of computer simulations, it was possible to postulate a probable reaction mechanism. In addition, the concentration changes of the transients and the final products were calculated as functions of time.

1. Introduction

The photolysis of prussic acid has been studied in the gas phase [1, 2]. Cyanohydrin, ammonia, formic acid and CO_2 in addition to H_2 and H_2O_2 have been produced as the final radiolysis products of CN^- ions in waste water [3 - 6]. At higher absorbed doses the formation of some amino acids and polymers has also been observed [7, 8], whereas in the presence of oxygen CNO^- is generated almost exclusively [9].

Prussic acid and some of its salts occur as undesired byproducts during aluminium manufacturing etc. and are used for example in electroplating procedures. The waste waters of such industries contain CN^- ions and exhibit an environmental load. Therefore an attempt was undertaken to investigate the photolysis of CN^- ions at 184.9 nm in aqueous alkaline solutions. Under these conditions CN^- ions absorb only negligibly [10]. Hence an attack of the primary products of water photolysis (H, e_{aq}^- and OH) on the substrate is expected. To obtain better understanding of the complicated competitive reactions, computer simulations were performed and were compared with the chemical analysis data.

2. Experimental

2.1. Light source and actinometry

A low pressure mercury lamp (Osram HNS 10 OZ) emitting at 184.9 and 253.7 nm was used in combination with a 4π-geometry irradiation vessel

as previously described [11, 12]. The light intensity I_0 at 184.9 nm was determined to be 4×10^{16} $h\nu$ ml^{-1} min^{-1} (25 °C) by measuring the hydrogen yield produced by the photolysis of methanol with a quantum yield $Q(H_2)$ of 0.83 [13]. Also 5 mol dm^{-3} of aqueous ethanol was employed, using a corrected value for $Q(H_2)$ of 0.4 (see later). The I_0 value obtained was in good agreement with that for methanol. The irradiation dose was varied from 2×10^{16} to 10^{17} $h\nu$ ml^{-1}.

2.2. Preparation of solutions

All chemicals (NaCN, NaOH and Ba(OH)$_2$·8H$_2$O, p.a. Merck, Darmstadt) were used without further purification. For the preparation of solutions of 10^{-2} - 5×10^{-2} mol dm^{-3} CN$^-$ ions at least triply distilled water was used. The pH value of 10 ± 0.1 was adjusted by means of a mixture of carbonate-free sodium and barium hydroxides. Before irradiation (at 25 °C) the solutions were saturated with oxygen-free argon or nitrogen (Oxygena, Vienna) for about 1 h.

2.3. Analysis

The CN$^-$ ion concentration was determined spectrophotometrically as the picrate at 520 nm [14] before and after irradiation. The formation of formaldehyde was followed by two methods. (1) Acidified 2,4-dinitrophenyl-hydrazine was added to the irradiated solution and the complex was extracted with CHCl$_3$ [15]. After concentrating the extract was chromatographed (on a thin layer of "Kieselgel G"; cyclohexane:ethyl acetate = 70:30) and the separated zones were scanned at 360 nm. (2) The formation of formaldehyde was followed using chromotropic acid and measuring the absorption at 570 nm [16]. Standard solutions were used for comparison. Cyanohydrin together with formaldehyde was determined at 412 nm in slightly basic media as the yellow acetylacetone complex [17]. The yield of formaldehyde was then substracted. The formate was first detected by thin layer chromatography ("Kieselgel G", C$_2$H$_5$OH:NH$_3$:H$_2$O = 80:4:16) using methyl red dye as an indicator. A quantitative evaluation of the spots was carried out by comparison with standard samples. Formate was also determined as the copper benzidine complex in acidic solution at 244 nm [18].

3. Results

The molar extinction coefficients ϵ at 184.9 nm for the three absorbing components (CN$^-$, OH$^-$ and H$_2$O) were measured by direct spectrophotometry and are shown in Table 1. It is obvious from the percentage absorption distribution that the light absorbed by 10^{-2} mol dm^{-3} CN$^-$ ions can be neglected.

The formation of the final products (NH$_3$, HCHO and HCOO$^-$) using aqueous 10^{-2} mol dm^{-3} CN$^-$ ions at pH 10 (25 °C) was studied as a function of the irradiation time. The initial quantum yields Q_i were calculated from

TABLE 1

Absorption distribution and molar extinction coefficient values
of UV light at 184.9 nm in the aqueous CN^--OH^- system

Component (mol dm^{-3})	$\epsilon_{184.9}$ (m^2 mol^{-1})	Absorption (%)
CN^- (10^{-2})	0.14	0.7
OH^- (10^{-4})	370	18.2
H_2O (55.55)	2.97×10^{-3}	81.1

the straight lines of the corresponding curves and are presented in Table 2.
For the consumption of CN^- ions at low UV doses a value for $Q(-CN^-)$ of
0.29 was determined. Theoretically computed Q values for the products are
also given in Table 2; a value for $Q(-CN^-)$ of 0.23 was obtained from these
results.

4. Computer simulations

Computer simulations were performed to obtain a more consistent
reaction mechanism for an explanation of the product formation. These
were based on the irradiation doses applied and on the quantum yields of the
primary photolytic products of water at pH 10. From Table 1 it is obvious
that the light at 184.9 nm is predominantly absorbed by water, leading to
the formation of H, OH and e_{aq}^-. Our previously reported quantum yields,
$Q(H,OH) = 0.36$ and $Q(e_{aq}^-) < 0.04$, for this reaction were based on the
aqueous 5 mol dm^{-3} ethanol actinometer with $Q(H_2) = 0.5$ [11, 12]. How-
ever, taking into consideration the corrections proposed by Bernas $et\ al.$
[19], a hydrogen yield $Q(H_2)$ of 0.4 is obtained for this actinometer, which
results in $Q(H,OH) = 0.29$ and $Q(e_{aq}^-) < 0.03$. These values seem to be more
reliable than those previously reported (see also ref. 20). Dainton and Fowles
[21] have reported a value for $Q(H,OH)$ of 0.30, established on $Q(-N_2O) =$
1.0, which is in very good agreement with the aforementioned value. For the

TABLE 2

Experimentally determined and computed initial quantum yields Q_i of products obtained
by the photolysis (184.9 nm) of aqueous 10^{-2} mol dm^{-3} CN^- ions at pH 10 (25 °C)

Product	Q_i values	
	Determined	Computed
NH_3	0.27	0.23
HCHO	0.07	0.087
$HCOO^-$	0.10	0.19

purpose of this work the values $Q(H,OH) = 0.3$ and $Q(e_{aq}^-) < 0.03$ were used. In addition a value for $Q(e_{aq}^-,OH)$ of 0.11 has been reported for the photolysis of OH^- ions [22].

For the computations the WR-16 programme of Schmidt [23, 24] was adapted for the CDC computer of the University of Vienna. The concentration changes of the short-lived species ($OH-\dot{C}=NH$, $H_2C=\dot{N}$ and $O=\dot{C}-NH_2$) and of the final products were calculated as functions of time. In this manner all reactions among the primary products (H, e_{aq}^- and OH), their attack on the CN^- ions and the subsequent hydrolysis steps of the transients were considered. The corresponding rate constants were taken from the literature [25]. The reactions of CN^- ions with the primary products of water photolysis are listed in Table 3.

The calculated data for the formation and consumption of the short-lived radicals for the steady state photolysis of CN^- ions (pH 10, 25 °C) are presented in Fig. 1 as functions of time. Figure 2 shows the time dependence of the product concentrations.

5. Discussion

The photolysis (184.9 nm) of CN^- ions of low concentration in slightly alkaline aqueous solutions (pH 10) is caused by the attack of the primary products of water (H, e_{aq}^- and OH) on the substrate. The final products were determined to be NH_3, HCHO and $HCOO^-$. CO_2 is also formed, but its

TABLE 3

Reactions of CN^- ions with H, e_{aq}^- and OH, the hydrolysis of the transients produced and the rate constants included in the computer programme

Number	Reactions	Rate constants (dm^3 mol^{-1} s^{-1})	Reference
1	$H + CN^- \rightarrow H\dot{C}=N^-$	3.6×10^7	26
2	$H\dot{C}=N^- + H_2O \rightarrow H_2C=\dot{N} + OH$	3.6×10^7	26
3	$e_{aq}^- + CN^- \rightarrow \dot{C}N^{2-}$	$<1 \times 10^6$	27
4	$\dot{C}N^{2-} + 2H_2O \rightarrow H_2C=\dot{N} + 2OH^-$	$<1 \times 10^6$	27
5	$H_2C=\dot{N} + H_2O \rightarrow H_2C=NH + OH$	$-^a$	29
6	$H_2C=NH + H_2O \rightarrow NH_3 + HCHO$	1×10^9	7
7	$OH + CN^- \rightarrow OH-\dot{C}=N^-$	7.1×10^9	26, 28
8	$OH-\dot{C}=N^- + H_2O \rightarrow OH-\dot{C}=NH + OH^-$	$(pK = 10.2)$	31
9	$OH-\dot{C}=NH \rightarrow O=\dot{C}-NH_2$	4×10^7	26
10	$O=\dot{C}-NH_2 + H_2O \rightarrow O=CHNH_2 + OH$	$-^a$	29
11	$O=CHNH_2 + H_2O \rightarrow NH_3 + HCOOH$	6.2×10^9	30

^{a}This rate constant could not be precisely computed because of the restrictions of the programme.

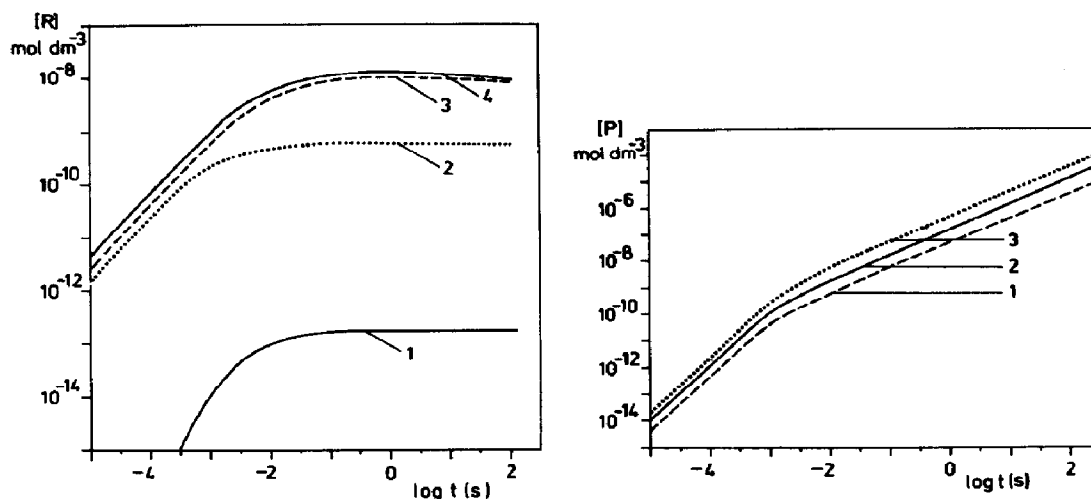Fig. 1. The formation and consumption of radicals as functions of time for steady state photolysis of the aqueous $CN^- - OH^-$ system: curve 1, $OH-\dot{C}=NH$; curve 2, $H_2C=\dot{N}$; curve 3, $O=\dot{C}-NH_2$; curve 4, total radical concentration.

Fig. 2. The formation of final products as a function of time for steady state photolysis of the aqueous $CN^- - OH^-$ system: curve 1, HCHO; curve 2, $HCOO^-$; curve 3, NH_3.

yield was not measured. The formation of CO_2 can explain the discrepancy between the determined and computed values of $Q(HCOO^-)$. Apart from this there is good agreement between the two series of Q values (Table 2). Hence it can be concluded that the postulated reaction mechanism for the formation of the final products is quite acceptable. Accordingly, the reactions of hydrogen atoms and e_{aq}^- with CN^- ions result first in the formation of the methylimino radical ($H_2C=\dot{N}$; reactions 2 and 4), which then hydrolyses to give NH_3 and HCHO. The resonance structure of $H_2\dot{C}=N$ is $HC=NH$ and has previously been observed using an electron spin resonance method [31].

The reaction of CN^- ions with OH is markedly dependent on the pH of the solution ($OH \rightleftharpoons O^- + H^+$, $pK = 11.9$; $HCN \rightleftharpoons CN^- + H^+$, $pK = 9.3$). According to reactions (7) - (11) given in Table 3, OH attack on CN^- ions leads to the production of the formamide radical, which finally results in NH_3 and HCOOH after a three-step hydrolysis.

It might be of interest to mention that a halide-like reaction, *i.e.*

$$CN^- + OH \longrightarrow CN^{\cdot} + OH^- \tag{12}$$

$$CN^- + CN \longrightarrow (CN)_2^- \tag{13}$$

has not been observed [32 - 34], but the formation of the formamide radical $O=\dot{C}-NH_2$ has been reported previously [28, 32 - 34]. Reaction (7) is therefore an addition step [35] and is followed by the acid-base reaction (8) and lactim-lactam rearrangement to give the formamide radical (reaction

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9). A general presentation of the rather complicated reaction mechanism is given schematically in Fig. 3.

Finally it should be noted that no polymer products were detected. This could be because of the relatively low CN^- ion concentration and the low UV doses employed.

The experimental and theoretical data obtained made it possible to explain the indirect photolysis of dilute aqueous CN^- ion solutions. For practical use of the CN^- ion photolysis, however, much higher quantum yields will be needed, which could be obtained for example by a sensitization process.
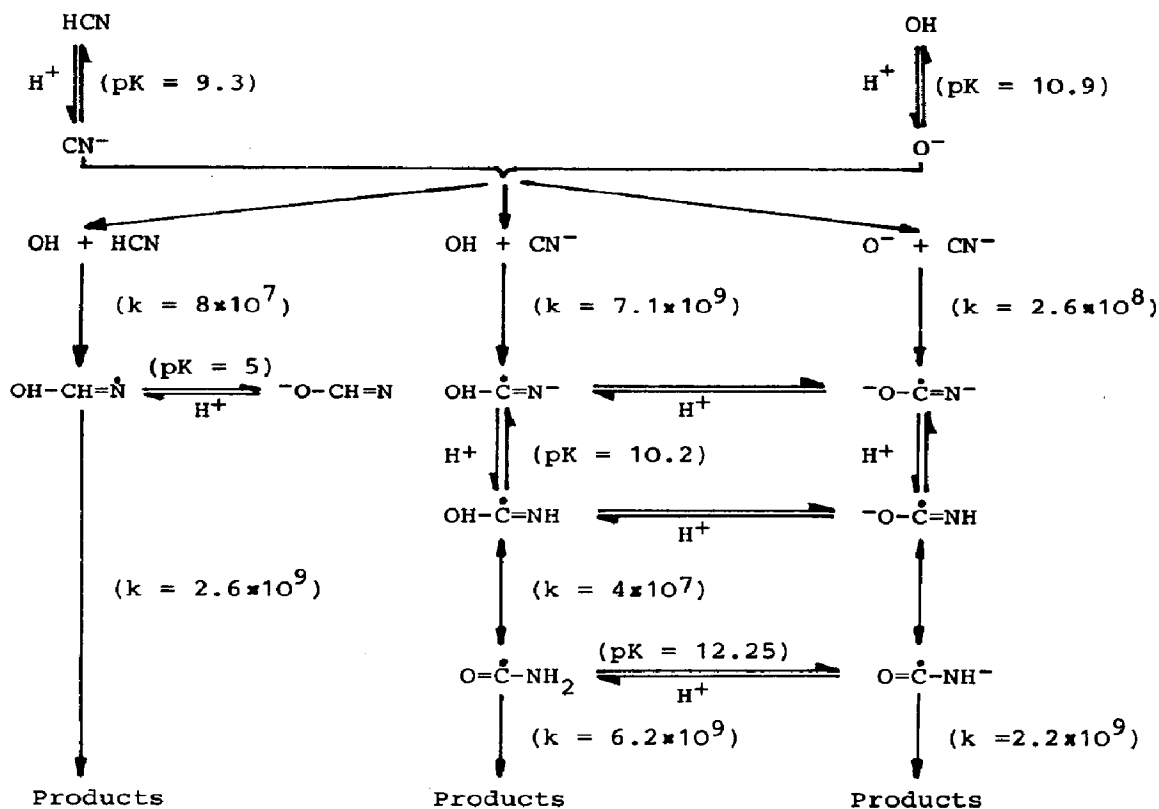

Fig. 3. Reactions of OH (or O^-) radicals with HCN and CN^- in aqueous solutions at various pH values (k values in units of $dm^3 \ mol^{-1} \ s^{-1}$).

References

1 I. Tokue, T. Urisu and K. Kuchitsu, *J. Photochem.*, *3* (1974) 273.
2 H. Mizutani, H. Mikuni and M. Takahashi, *Chem. Lett.*, (1972) 573.
3 H. Ogura, *J. Radiat. Res.*, *8* (1967) 93.
4 H. Ogura and M. Kondo, *Bull. Chem. Soc. Jpn*, *40* (1967) 2448.
5 A. Yakohata and S. Tsuda, *Doitai To Hoshasen*, *4* (1961) 393.
6 H. Ogura, T. Fujimura, S. Murozono, K. Hirano and M. Kondo, *J. Nucl. Sci. Technol.*, *9* (1972) 339.
7 Z. D. Draganic, I. G. Draganic and M. Borovicanin, *Radiat. Res.*, *66* (1966) 42.
8 M. A. Sweeny, A. P. Toste and C. Ponnamperuma, *Origins Life*, *7* (1976) 4.
9 R. G. Arshakuni, S. S. Chirkinyan, I. A. Gambaryan, L. M. Marochkina, P. I. Dolin and R. V. Dzhagatspanyan, *High Energy Chem.*, *5* (1974) 475.
10 R. P. Buck, S. Singhadeja and L. B. Rogers, *Anal. Chem.*, *26* (1954) 1240.
11 N. Getoff, *Monatsh. Chem.*, *99* (1968) 136.
12 N. Getoff and G. O. Schenck, *Photochem. Photobiol.*, *8* (1968) 167.
13 C. von Sonntag, *Tetrahedron Lett.*, *25* (1969) 5853.
14 F. B. Fisher and J. S. Brown, *Anal. Chem.*, *24* (1952) 1440.
15 G. R. A. Johnson and G. Scholes, *Soc. Anal. Chem.*, *22* (1954) 1426.
16 D. A. MacFayden, *J. Biol. Chem.*, *158* (1945) 107.
17 T. Nash, *Biochem. J.*, *55* (1955) 416.
18 Z. D. Draganic, *Anal. Chim. Acta*, *28* (1963) 394.
19 A. Bernas, M. Bodard and D. Saghattchian, *J. Chim. Phys. Phys.-Chim. Biol.*, *62* (1965) 1418.
20 C. von Sonntag and H.-P. Schuchmann, *Adv. Photochem.*, *10* (1977) 59.
21 F. S. Dainton and P. Fowles, *Proc. R. Soc. London, Ser. A*, *287* (1965) 295.
22 F. S. Dainton and P. Fowles, *Proc. R. Soc. London, Ser. A*, *287* (1965) 312.
23 K. H. Schmidt, *ANL-7100 (TID-4560), ARC Research and Development Rep.*, 1966.
24 K. H. Schmidt, *J. Phys. Chem.*, *81* (1977) 1257.
25 M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isot.*, *18* (1967) 493.
26 H. Büchler, R. E. Büchler and R. Cooper, *J. Phys. Chem.*, *80* (1976) 1549.
27 M. Anbar and E. J. Hart, *J. Phys. Chem.*, *69* (1965) 973.
28 Z. D. Draganic, I. G. Draganic and V. Niketic, *Radiat. Res.*, *69* (1977) 223.
29 K. J. Hartig, *Dissertation*, University of Vienna, Austria, 1979.
30 D. Behar, *J. Phys. Chem.*, *78* (1974) 2660.
31 D. Behar and R. W. Fessenden, *J. Phys. Chem.*, *76* (1972) 3945.
32 I. G. Draganic, Z. D. Draganic and R. A. Holroyd, *J. Phys. Chem.*, *75* (1971) 608.
33 I. G. Draganic, Z. D. Draganic, L. Petkovic and A. Nikolic, *J. Am. Chem. Soc.*, *95* (1973) 7193.
34 I. G. Draganic, Z. D. Draganic and U. Markovic, *Int. J. Radiat. Phys. Chem.*, *8* (1976) 339.
35 I. Kraljic and C. N. Trumbore, *J. Am. Chem. Soc.*, *87* (1965) 2547.