Effects of Alkaline Ferrocyanide on Non-faradaic Yields of Anodic Contact Glow Discharge Electrolysis: Determination of the Primary Yield of OH˙ Radicals

Rajeshwar Singh · Urvashi Gangal · Susanta K. Sen Gupta

Abstract Non faradaic yields of anodic contact glow discharge electrolysis (CGDE) originate through H˙ and OH˙ radical generated during the process. Scavenging effects of $Fe(CN)_6^{4-}$ on OH˙ radicals, in alkaline media have been investigated. A kinetic analysis of the competing reactions of O^- with different species in the system leads to an yield of 9.8 mol mol electron^{-1} of OH˙ and H˙ radicals each in the liquid phase reaction zone of anodic CGDE in good agreement with the yield reported from a study involving H˙ radical scavengers.

Keywords Contact glow discharge electrolysis · OH˙ scavenger · Alkaline ferrocyanide · Non-faradaic yields · Primary radical yield

Introduction

Contact glow discharge electrolysis (CGDE) or plasma electrolysis (PE) is a non-conventional electrolysis in which a luminous sheath of plasma is sustained by DC glow discharges between an electrode and the liquid electrolyte around it. The phenomenon develops spontaneously at either the anode or the cathode during normal electrolysis (NE) at high enough voltages in aqueous, non-aqueous or molten electrolytes. The electrode, where the current density is larger, the electrolyte resistivity is higher or the electrolyte surface tension is lower, becomes the centre of CGDE. The critical voltage for the onset of full CGDE, called the mid-point voltage, is 420 V for the anode and 160 V for the cathode in aqueous electrolytes [1, 2]. The mechanism for NE-to-CGDE transition at the anode in an aqueous electrolyte has been elucidated to consist of the sequences: normal electrolysis, Joule heating vaporization near the anode, formation of a stable two-phase flow between the vapour bubbles escaping away from the anode and the liquid anolyte moving towards it, collapse of this flow pattern and formation of an unstable vapour film over the anode with an overlying heavier liquid, stabilization of the vapour film and incipience of glow

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discharges across the film. The field over this vapour plasma film at the anode, 8–40 MV m^{-1} is sufficient to sustain visible glow discharges inside it [3, 4]. A highly remarkable aspect of chemical results of CGDE is their strong deviation from the yield expected according to the Faraday's law [1, 5–8]. Further, the products contain species novel for normal electrolysis. Thus, the yields of anodic CGDE at 450 V in an aqueous inert-type electrolyte like K_2SO_4, K_2HPO_4 etc. comprise around 2 mol mol electron^{-1} of H_2, 0.5 mol mol electron^{-1} of H_2O_2 and 1 mol mol electron^{-1} of O_2 as compared to the faradaic yield of 0.25 mol mol electron^{-1} of O_2 [8]. It has been shown that the yields over and above the faradaic one, the nonfaradaic yields originate in two reaction zones of anodic CGDE, the liquid-phase near the plasma anolyte interface and the plasma around the anode. Further, nearly 80% of the nonfaradaic yields originate in the liquid-phase reaction zone where sufficiently energized $H_2O_{gas}^+$ ions from the anode plasma will each break up several liquid H_2O molecules into H$^.$ and OH$^.$ radicals [7, 8]. The formation of these radicals in the anolyte during anodic CGDE was proved by an ESR study using 5,5-dimethyl pyrroline-1-oxide (DMPO) as the spin trap [9, 10]. The radicals initiate several reactions to give rise to considerable yields of H_2, H_2O_2 and O_2^E there by a radiolytic mechanism [7, 8]. The potentiality of anodic CGDE as a tool for generating radicals in high local concentrations has been amply demonstrated by examples of its applications in the synthesis of hydrazine from ammonia [1, 11], oxalic acid from formic acid [12], polyacrylamide from acrylamide [13, 14], glycine and α-alanine from ammonia and carboxylic acids [15] and in the degradation of polymers [16], dipeptides [17] and of organic contaminants in waste waters [18–30]. Obviously, it needs developing a method for determining conveniently the primary yield of H$^.$/OH$^.$ radicals in the liquid-phase reaction zone of anodic CGDE. The mechanism of nonfaradaic chemical effects of anodic CGDE being understood [7, 8], an investigation based on the competition kinetics of the reactions involving H$^.$/OH$^.$ and an appropriate radical scavenger in the anolyte is a straight approach towards this objective. An earlier attempt of ours in this direction based on the use of Ce^{3+} ion as the OH$^.$ scavenger gave an estimate of 12.8 mol mol electron^{-1} as the primary yield of OH$^.$ radicals [31]. However, the method needed applying corrections due to reduction of the oxidised product, Ce^{4+} by H_2O_2. Recently, we employed a method based on the use of a number of H$^.$ scavengers in which no such correction need be applied, led to an yield as 9.8 mol of H$^.$ radicals for each mol electron of electricity [32] For further substantiation of this result, it is worth examining a determination involving an OH$^.$ scavenger which neither itself nor its oxidized form would react with H_2O_2. More desirable would be if its oxidised form does not get reduced by H$^.$ radicals during CGDE. Alkaline $Fe(CN)_6^{4-}$ is the OH$^.$ scavenger of choice for the purpose:

$$OH^. + OH^- \rightleftharpoons O^- + H_2O \qquad (1a)$$

$$O^- + Fe(CN)_6^{4-} \xrightarrow{H_2O} Fe(CN)_6^{3-} + 2OH^- \qquad (1b)$$
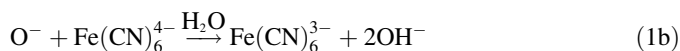
Owing to inherent instability of H_2O_2 in alkaline solutions [33] no complications due to oxidation of $Fe(CN)_6^{4-}$ or reduction of $Fe(CN)_6^{3-}$ by H_2O_2 could arise. Further, there was observed no reduction of $Fe(CN)_6^{3-}$ during CGDE of its alkaline solutions. Further, for formation of $Fe(CN)_6^{3-}$ by anodic CGDE, even 0.006 M $Fe(CN)_6^{4-}$ would suffice unlike that for Ce^{4+} which needs a Ce^{3+} solution of 0.02 M concentration. Here, we discuss the results of non-faradaic oxidation of alkaline $Fe(CN)_6^{4-}$ and report the findings on the primary yield of OH$^.$ radicals by anodic CGDE.

Experimental

The cell set up employed for studying the effect of alkaline $Fe(CN)_6^{4-}$ on nonfaradaic chemical effects of anodic CGDE is a symmetrical H-type Corning divided cell (height, 11 cm; dia., 30 mm) having a bridge of length 7.5 cm (internal dia. 15 mm) with a G-5 sinter glass disc diaphragm at 1.5 cm height from base of the cell, fitted with a platinum wire anode (length 5 mm, dia. 0.35 mm) and a platinum foil cathode (1×1 cm², 0.20 mm thickness) along with necessary facilities for collecting both the electrode gases and the electrolysed solutions from either electrode compartment as described in Fig. 1a; anolyte, 0.01 M K_2SO_4 containing $K_4Fe(CN)_6$ at different (0.006–0.06 M) concentrations: catholyte, 0.05 M K_2SO_4 mixed with 0.02 M H_2SO_4; ambient temperature, 80 ± 5°C; pressure, atmospheric; voltage applied, 450 V; current passed, 35 ± 5 mA. Photographs of the anode during NE and anodic CGDE are shown in Fig. 1b.

Power was supplied from an Aplab 7323 medium voltage DC regulated power supply which provided a maximum of 1 A at voltages up to 1 kV. Current and voltages were measured using an OSAW multirange milliammeter and an Alcock multirange voltmeter, respectively. Quantities of electricity passed were measured by a pre-calibrated URJA digital coulometer. The gaseous products of anodic CGDE were analysed quantitatively in a precision model Haldane-type gas analyser. The anode gas was analysed for O_2 by absorption in alkaline pyrogallol, and H_2 by slow combustion in excess of O_2 on a red hot platinum spiral following a standardised procedure. The anolyte from anodic CGDE after necessary acidification with 2 M H_2SO_4 was analysed for unreacted $Fe(CN)_6^{4-}$ by titration with a standard (0.025–0.1 M) solution of ceric ammonium sulphate following a standard procedure [34]. The results thus obtained on determination of $Fe(CN)_6^{3-}$ yield were verified by parallel absorbance measurements of $Fe(CN)_6^{3-}$ at 420 nm (absorptivity, 10^3 L mol⁻¹ cm⁻¹) in a 160 A Shimadzu UV–VIS spectrophotometer. It may be noted during anodic CGDE of $K_3[Fe(CN_6)]$ solutions under otherwise similar conditions, concentration of $Fe(CN)_6^{3-}$ was found unchanged.

Results and Discussion

As shown in Table 1, non-faradaic yields at the glow discharge anode during CGDE of 0.06 M $K_4Fe(CN)_6$ basified with 0.1 M KOH comprise H_2 (2.58 ± 0.01 mol mol electron⁻¹) and an equivalent amount of $Fe(CN)_6^{3-}$, Y_{Ex} (1.52 ± 0.01 mol mol electron⁻¹) plus 0.91 ± 0.01 mol mol electron⁻¹ of O_2, Y_{O_2E}. The latter two are over and above the faradaic yields of 0.48 ± 0.01 mol mol electron⁻¹ of $Fe(CN)_6^{3-}$ and 0.13 ± 0.01 mol mol electron⁻¹ of O_2 obtained under normal electrolytic conditions (Table 1). A comparison between the non-faradic yields from 0.1 M KOH anolyte with and without $Fe(CN)_6^{4-}$ (Table 1) shows that the yield Y_{Ex} is obtained at the cost of that of O_2^E indicating scavenging action of $Fe(CN)_6^{4-}$ for OH˙ radicals.

$Fe(CN)_6^{4-}$ may also inhibit the reaction,

$$O^- + H˙ \rightarrow OH^- \tag{2}$$

and enhance the yield of H_2 at the anode (Table 1).

The nonfaradaic yield (Y^E) of $Fe(CN)_6^{3-}$ for a given concentration of $Fe(CN)_6^{4-}$ was found linearly increasing with quantities of electricity (q) passed as shown in Fig. 2.
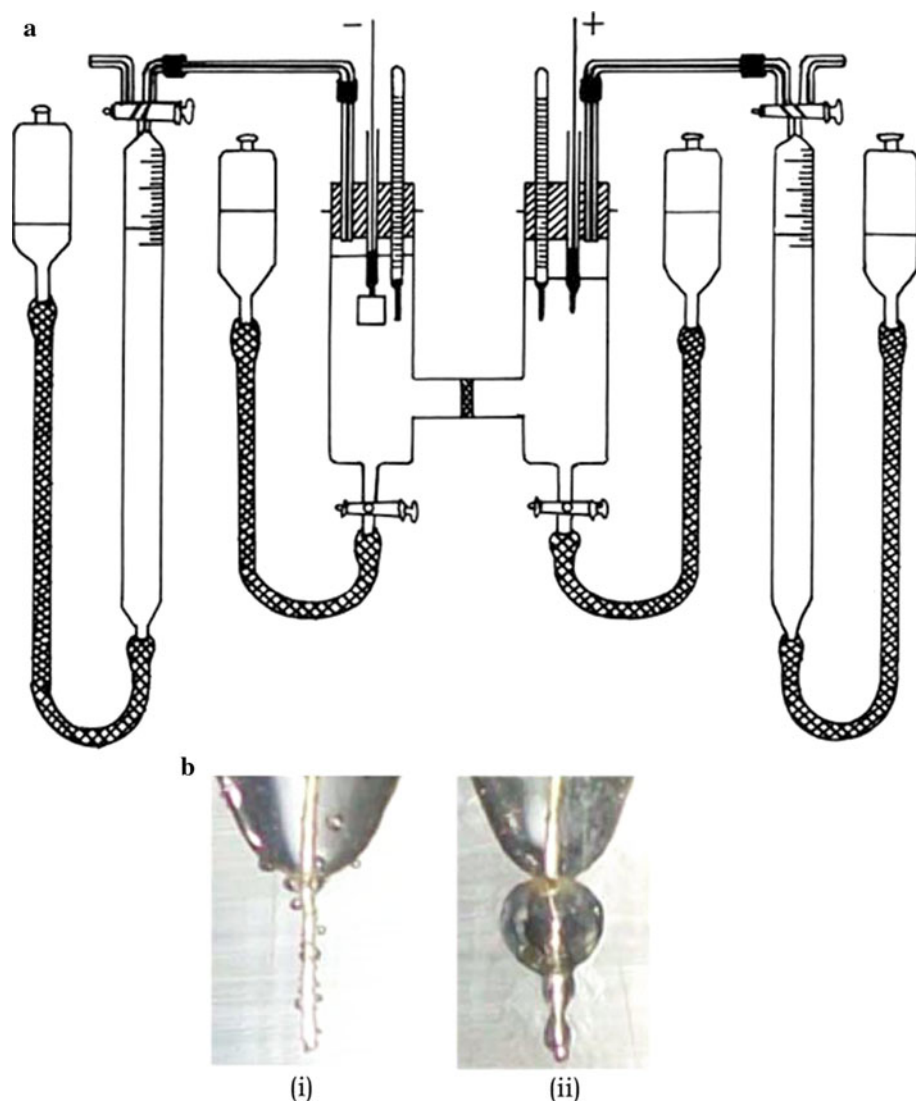
Fig. 1 **a** A schematic drawing of the cell setup used for studying anodic CGDE. **b** Photographs of the anode during (i) NE and (ii) CGDE

A very useful way of expressing this yield is by quoting its differential yield, G(/mol mol electron^{-1}) obtained as the slope of the tangent to the yield versus q curve. The values of $G\left(Fe(CN)_6^{3-}\right)$ obtained at different concentrations $Fe(CN)_6^{4-}$ (Table 2) show clearly that G rose with concentration approaching finally a limiting value (Fig. 3). The results obtained are discussed in the following.

According to the radiolytic mechanism [7, 8], $H_2O_{gas}^+$ ions generated in the anodic plasma get sufficiently energized while entering the liquid anolyte across the steep cathode fall (~ 8 kV cm^{-1}) at the plasma | anolyte interface. These energized $H_2O_{gas}^+$ ions will each bombard several liquid water molecules there to dissociate them into H$^{\cdot}$ and OH$^{\cdot}$ radicals,

Table 1 Effect of $Fe(CN)_6^{4-}$ on nonfaradaic yields of anodic CGDE in alkaline media at 20C (20.7×10^{-5} mol electron) of electricity

Anolyte	V_A (ml)	Y (mol mol electron^{-1}) ± 0.01	Y_{NE} (mol mol electron^{-1}) ± 0.01	Y_{Ex} (mol mol electron^{-1}) ± 0.01	Y_{H_2} (mol mol electron^{-1}) ± 0.01	Y_{O_2} (mol mol electron^{-1}) ± 0.01	$Y_{(O_2)_{NE}}$ (mol mol electron^{-1}) ± 0.01	$Y_{O_2}^E$ (mol mol electron^{-1}) ± 0.01
0.1 M KOH	15.3	–	–	–	2.04	1.26	0.25	1.01
0.1 M KOH + 0.06 M K$_4$Fe(CN)$_6$	16.8	2.00	0.48	1.52	2.58	1.04	0.13	0.91

V_A Volume of anode gas at NTP, Y Yield of Fe(CN)$_6^{3-}$, Y_{NE} Yield of Fe(CN)$_6^{3-}$ by normal electrolysis at 60 V, Y_{Ex} Yield of Fe(CN)$_6^{3-}$ in excess of Y_{NE}, Y_{H_2} Yield of anodic H$_2$, Y_{O_2} Yield of anodic O$_2$, $Y_{(O_2)_{NE}}$ Yield of O$_2$ by normal electrolysis, $Y_{O_2}^E$ Yield of O$_2$ in excess of $Y_{(O_2)_{NE}}$
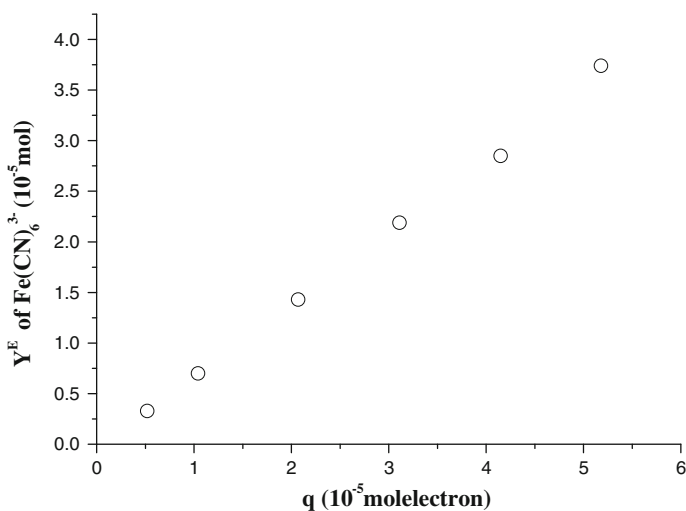
Fig. 2 Non faradaic Yield (Y^E) of $Fe(CN)_6^{3-}$ versus quantity of electricity (q)

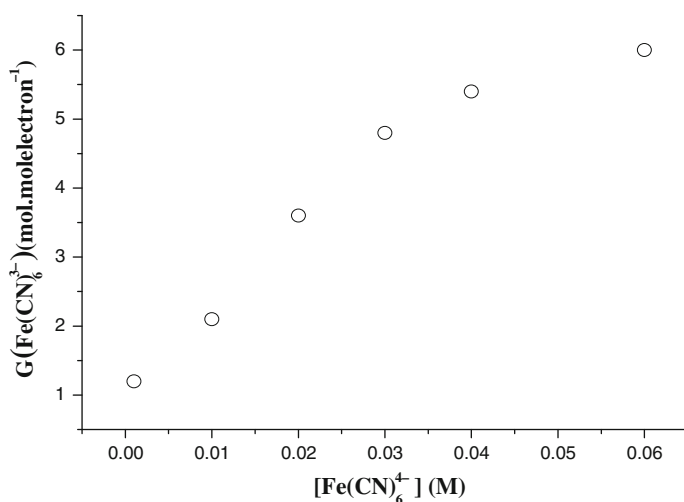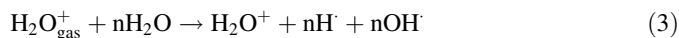| **Table 2** Variation of $G\left(Fe(CN)_6^{3-}\right)$ with $[Fe(CN)_6^{4-}]$ during anodic CGDE of $K_4Fe(CN)_6$ solutions	$[Fe(CN)_6^{4-}]$ (M)	$G\left(Fe(CN)_6^{3-}\right)$ (mol mol electron^{-1})
	0.001	1.2
	0.01	2.1
	0.02	3.6
	0.03	4.8
	0.04	5.4
	0.06	6.0

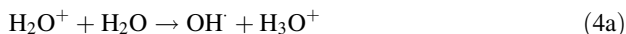**Fig. 3** Variation of $G(Fe(CN)_6^{3-})$ with $[Fe(CN)_6^{4-}]$ during anodic CGDE of alkaline ferrocyanide solutions

$$H_2O^+_{gas} + nH_2O \rightarrow H_2O^+ + nH^. + nOH^. \tag{3}$$

besides breaking up one more H_2O molecule by normal charge transfer to produce one further $OH^.$,

$$H_2O^+ + H_2O \rightarrow OH^. + H_3O^+ \tag{4a}$$

The $OH^.$ radicals generated through the reaction (Eq. 4a, 4b) give rise subsequently to faradaic yield of O_2,

$$OH^. + OH^. \rightarrow 1/2\,O_2 + H_2O \tag{4b}$$

whereas $H^.$ and $OH^.$ radicals produced through the reaction (Eq. 3) give rise to H_2, H_2O, H_2O_2 and O_2^E in the liquid-phase reaction zone,

$$H^. + H^. \rightarrow H_2 \tag{5}$$

$$H^. + OH^. \rightarrow H_2O \tag{6}$$

$$OH^. + OH^. \rightarrow H_2O_2 \tag{7}$$

$$OH^. + H_2O_2 \rightarrow HO_2^. + H_2O \tag{8a}$$

$$OH^. + HO_2^. \rightarrow O_2 + H_2O \tag{8b}$$

In the presence of alkali, owing to the formation of O^- (Eq. 1a) the reactions (Eqs. 6–8b) transform respectively to Eq. 2 and

$$O^- + OH^. \rightarrow HO_2^- \tag{9}$$

$$HO_2^- + OH^. \rightarrow O_2^- + H_2O \tag{10a}$$

$$O_2^- + OH^. \rightarrow O_2 + OH^- \tag{10b}$$

and the scavenging action of $Fe(CN)_6^{4-}$ for $OH^.$ occurs as Eq. 1b [33].

Determination of the Primary Yield of Radicals Produced in Anodic CGDE

The primary yield of $OH^.$ radicals generated during anodic CGDE in its liquid-phase reaction zone can be determined employing the principle of competition kinetics for a reaction scheme involving $OH^.$ only. Since, in an alkaline medium, $OH^.$ acts effectively as O^-, the scheme involves the reactions 1a, 1b, 2 and 9 only. If K_{o-} represents the equilibrium constant of the reaction 1a and k_1, k_2 and k_9 the rate constants of the reactions 1b, 2 and 9 respectively, an $OH^.$ in an alkaline solution would undergo, the yield, G of $Fe(CN)_6^{3-}$ in mol mol electron^{-1} can be expressed as

$$G\left(Fe(CN)_6^{3-}\right)$$
$$= n \frac{k_1 K_{O^-}[OH^-][OH^.]\left[Fe(CN)_6^{4-}\right]}{k_1 K_{O^-}[OH^-][OH^.]\left[Fe(CN)_6^{4-}\right] + k_2 K_{O^-}[OH^-][OH^.][H^.] + k_9 K_{O^-}[OH^-][OH^.]^2} \tag{11}$$

where n stands for the primary yield of $OH^.$ radicals in mol mol electron^{-1}. Equation (11) can be re-expressed as

$$G\left(Fe(CN)_6^{3-}\right) = n \frac{\left[Fe(CN)_6^{4-}\right]}{\left[Fe(CN)_6^{4-}\right] + A + B} \qquad (12)$$

where $A = \frac{k_2}{k_1}[H^.]$ and $B = \frac{k_9}{k_1}[OH^.]$.

Concentration of the radicals $H^.$, $OH^.$ will change as they advance into the bulk anolyte. The kinetic situation in the liquid-phase reaction zone is thus very complex and requires a complete knowledge of concentration profiles of the reactive species over the reaction zone for its solution. However, the application of simplifications where A and B (Eq. 12) in the steady state can be regarded as approximately constant justifiably for $Fe(CN)_6^{4-}$ scavenger which has low enough k_1 ($<7 \times 10^7$ M^{-1} s^{-1}) as compared to k_2 ($1{,}300 \times 10^7$ M^{-1} s^{-1}) and k_9 ($<2{,}600 \times 10^7$ M^{-1} s^{-1}) [33], leads to results of significant interest.

Interestingly $G(Fe(CN)_6^{3-})$ versus $Fe(CN)_6^{4-}$ plot (Fig. 1) exhibits a growth pattern as predicted by Eq. (12). Further, results of single rectangular hyperbolic regression analysis of $G\left(Fe(CN)_6^{3-}\right)$ data on $[Fe(CN)_6^{4-}]$ (Table 2) are statistically well significant:

$$G\left(Fe(CN)_6^{3-}\right) = 9.77 \frac{\left[Fe(CN)_6^{4-}\right]}{\left[Fe(CN)_6^{4-}\right] + 0.03} \qquad (n = 6, R = 0.994) \qquad (13)$$

which explains 98.9% of the variance with F(356.23)-level of significance on the correlation coefficient (R) better than 0.1% and t level of significance on n and (A + B) better than 0.05 and 0.5% respectively.

The primary radical yield (n) of anodic CGDE thus obtained using $Fe(CN)_6^{4-}$ as the $OH^.$ scavenger, 9.8 mol mol electron^{-1} conforms to the result 10 mol mol electron^{-1} determined by the previous method based on the use of $H^.$ scavengers.

The yield of CGDE at the glow discharge anode in an inert-type electrolyte could go as high as 5 mol of H_2 plus 2.75 mol of O_2 for each mol electron of electricity as against 0.25 mol of O_2 by normal electrolysis.

Conclusions

Remarkably excess chemical yields of anodic CGDE in aqueous media over and above that expected on the basis of the Faraday's law originate mainly through liquid-phase phase reactions triggered by $H^.$ and $OH^.$ radicals. These radicals are generated by bombardment of sufficiently energized $H_2O_{gas}^+$ ions emerging from the plasma around the anode, on liquid water molecules at the plasma | anolyte interface. An attempt for determining the primary yield of $OH^.$ radicals has been made on the basis of a kinetic scheme of competing reactions of the radicals with alkaline $Fe(CN)_6^{4-}$ as the scavenger and the yield was found to be ~ 10 mol mol electron^{-1}. This compares well with that of $H^.$ radicals obtained by using $H^.$ scavengers.

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