IMPURITIES IN CERTAIN PHOTO-CHEMICAL SYSTEMS INVOLVING RADICALS IN AQUEOUS SOLUTION

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HABER AND WEISS[1,2] explained that the Fenton's reaction of hydrogen peroxide—ferrous ion involved hydroxyl radicals. Kolthoff and Medalia,[3,4] in a study of oxidation of ethyl alcohol by the system, H_2O_2-Fe^{2+}, established that micro concentrations of inorganic and organic impurities in distilled water or the reagents used in the system gave rise to induced oxidation of ferrous ions. Simultaneously and independently the significance of such impurities in distilled water were recognised by Barb, Baxendale, George and Hargrave,[5] in the oxidation of leuco form of Aeronol brilliant Blue by the Fenton's reagent. In this connection, the work of Fricke and Hart[6,7] who showed long ago that the traces of organic impurities in distilled water could be quantitatively removed only by irradiation with X-rays may also be recalled. A qualitative evidence for the effect of organic impurities in the photochemical system, ion-pair complex, $Fe^{+3}X^-$—Vinyl Monomer, M, where $X^- = OH^-$, Cl^-, N_3^- etc. and M = acrylonitrile or methylmethacrylate or methacrylic acid, has been inferred in this paper.

EXPERIMENTAL AND RESULTS

When the system $Fe^{+3}X^-$-M, is irradiated with ultraviolet light of wavelength 300-400 mμ, the primary photochemical reaction is an electron transfer reaction involving reduction of the cation and oxidation of the anion to a free radical[8,9] In a secondary reaction free radicals initiate polymerization of the substrate, vinyl monomer. A detailed kinetic study of polymerization with experimental details was presented by Evans, Santappa and Uri[10] and Santappa.[11] Experiments were mostly carried out with 313 mμ The reaction system, $Fe^{+3}X^-$-M, in aqueous solution has been deaerated by nitrogen purified in Fieser's[12] solution. The intensity of light (I) was determined actinometrically using uranyl oxalate solution. The light absorption fraction, k_e, by the ion-pair species was determined spectrophotometrically. After irradiation of the system and filtration of the polymer, the rate of ferrous ion production (dFe^{+2}/dt) was determined colorimetrically using o-phenanthroline as the colouring and complexing agent.

It was observed that the systems, $Fe^{+3}OH^-$-M and $Fe^{+3}Cl^-$-M, gave constant quantum yields

for ferrous ion, 0.05, and 0.13 respectively with big or small concentrations of monomer. The quantum yields in these two cases did not decrease even in the absence of monomer. On the other hand, with the system, $Fe^{+3}N_3^-$-M, a linear variation of quantum yield for ferrous ion with monomer concentration and a maximum quantum yield of 0.5 for high concentrations of the monomer was observed (Fig. 1).
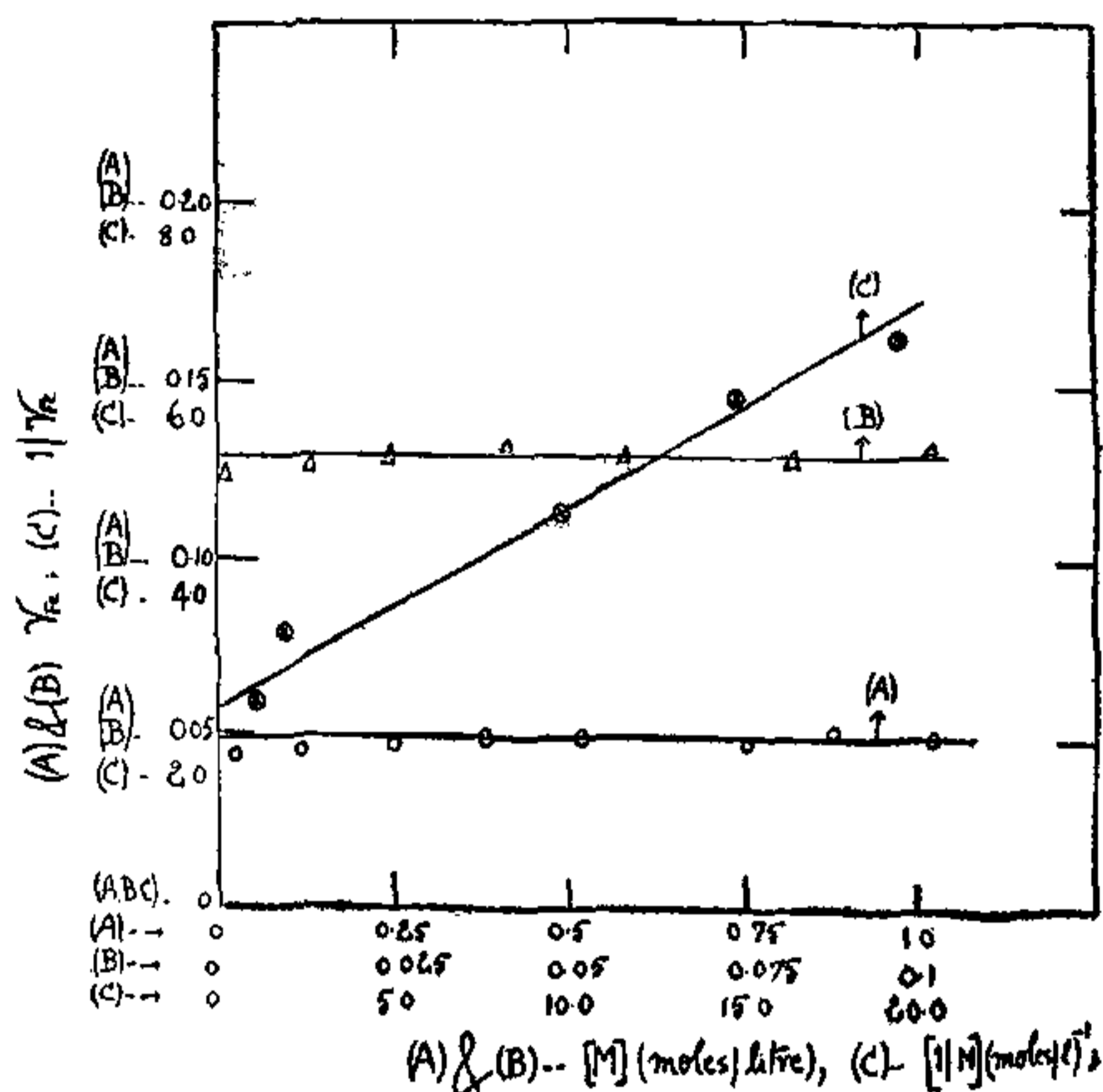

FIG. 1. Graph A represents the invariability of quantum yields for ferrous production (γ_{Fe}) with monomer concentration in the system Fe^{+3} OH^- —acrylo nitrile, Graph B represents the same invariability in the system Fe^{+3} Cl^--methyl-methacrylate; Graph C represents variation of reciprocal quantum yield with reciprocal monomer concentration in the system Fe^{+3} N_3^-. acrylo-nitrile at pH = 1 to 11.

The sources from which impurities might be introduced into the reaction system are (1) Fieser's solution which is used to deoxygenate nitrogen which bubbled through the reaction cell. (2) The reagents like water, ferric perchlorate, perchloric acid, hydrochloric acid, sodium azide, etc., which are used in the system.

Three methods of deaeration indicated in Table I by (a), (b), (c) were tried and it is obvious from Table I that it makes a great difference in the rate of ferrous ion production between these methods. It was also observed that the rate of ferrous ion production was

unaffected by change of monomer concentration using either (b) or (c) type of deaeration.

TABLE I

Method of deaeration	Ion Pair	313 mμ ; I=1·2×10^{-4} N$h\nu$/hr. dFe^{+2}/dt (moles/hr.) ×10^6		365 mμ ; I=7×10^{-5} N$h\nu$/hr. dFe^{+2}/dt (moles/hr.) ×10^6	
		Monomer	No Monomer	Monomer	No Monomer
(a)	Fe^{+3} OH$^-$	1·75	1·2		
	Fe^{+3} Cl$^-$	3·1	2·0	1·7	1·4
(b)	Fe^{+3} OH$^-$	8·0	8·0	3·7	3·7
	Fe^{+3} Cl$^-$	1·6	1·6	9·0	9·0
(c)	Fe^{+3} OH$^-$	8·0	5–8	3·6	2·8–3·6
	Fe^{+3} Cl$^-$	14·0	12–14	8·2	7·6–8·2

(a) No distilled water or monomer solution between Fieser's solution and reaction cell. *(b)* Distilled water or monomer solution between Fieser's solution and reaction cell. *(c)* Degassing the system by high vacuum.

A few experiments were conducted along lines which facilitated destruction of organic impurities if any in the system and accumulation of ferrous ion, before adding monomer to the system. The solutions containing (1) the ion-pair, and (2) the monomer were first taken in separate compartments of the reaction system which was thoroughly deaerated by (b) or (c) method. Then the compartment containing ion-pair solution alone was irradiated with a strong source of U.V light and ferrous ion produced was estimated. The monomer solution *from the second compartment was added to* the already irradiated ion-pair solution and the combined solution was further irradiated. From the total ferrous ion produced it was possible to calculate ferrous ion produced due to various concentrations of monomer (Table II).

TABLE II

Ion-Pair:Fe^{+3}Cl$^-$; [Fe^{+3}]=10^{-3} M; [HCl]=0.5 N Monomer = Methyl methacrylate

| [M] Molar	Concentration [Fe^{+2}] ×10^4		
	Accumulated before adding monomer	Total after adding monomer	due to monomer
0·1	0·87	3·16	2·28
0·1	3·42	3·75	0·33
0·1	2·06	2·73	0·67
0·01	2	3·56	1·56
0·001	1·26	4·0	2·74
0	0·5	0·575	0·075

It is seen from Table II that the results were not reproducible for the same concentration of the monomer nor is there any regularity in variation of ferrous ion produced with the change in monomer concentration. The only difference in experimental conditions was that different samples of distilled water were used for each experiment. Various types of distilled water, *e.g.*, (a) chemically pure water distilled over KMnO$_4$ and used after a fortnight; (b) water distilled over KMnO$_4$ and used immediately, and (c) conductivity water, were then used in the system, Fe^{+3} Cl-methylmethacrylate, which was irradiated under identical conditions. These gave different values for the rates of ferrous ion production.

DISCUSSION

Assuming stationary concentrations for free radicals which initiate and propagate polymerization (k_i is the rate constant for initiation) one can obtain the following expression for the rate of ferrous ion production,

$$\frac{d\text{Fe}^{+2}}{dt} = \frac{k_s k_e I}{k_d + k_s} \left(\frac{k_i [M]}{k_0 [\overline{\text{Fe}^{+2}}] + k_i [M]} \right)$$

where k_s is the rate constant for separation of Fe^{+2}X into Fe^{+2} + X; k_d and k_0 are constants for the following primary and secondary dark back reactions respectively. I is the intensity of light.

$$\text{Fe}^{+2}\text{X} \xrightarrow{k_d} \text{Fe}^{+3}\text{X}^-$$

$$\text{Fe}^{+2} + \text{X} \xrightarrow{k_0} \text{Fe}^{+3} + \text{X}^-$$
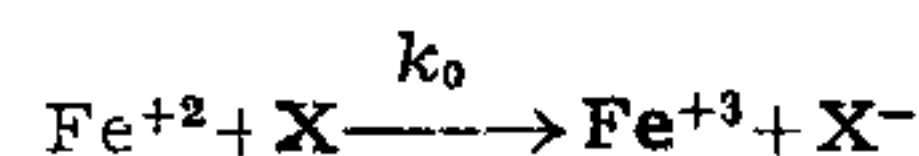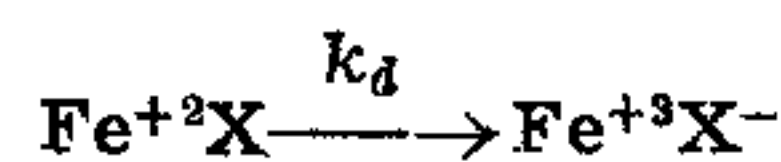
The net quantum yield for ferrous ion production should linearly vary with concentration of the monomer attaining a maximum value represented by $k_s/(k_s + k_d)$ for high concentrations of monomer when $k_i [M] \gg k_0 [\text{Fe}^{+2}]$. One possible explanation that suggests itself for the constant quantum yields of ferrous ion with Fe^{+3}OH$^-$ and Fe^{+3}Cl$^-$ ion-pairs even in the absence of any monomer, is that organic impurities in the system react with hydroxyl or chloride radicals and thus prevent dark back reactions. The assumption of existence of impurities seems justified because varying quantum yields were obtained with different samples of distilled and conductivity waters under identical experimental conditions. The impurities in other reagents in the system, ferric perchlorate, perchloric acid, and hydrochloric acid may also cause these discrepancies. All the reagents, however, have been tested to be free from any oxidising or reducing impurities. On the other hand, by using same sample of water for any set of experiments and using maximum concentration of

monomer it was possible to reduce the interference of the impurities to the minimum. That the azide radicals appear to be particularly stable towards these impurities might be understood by their resonance stabilization among the structures,
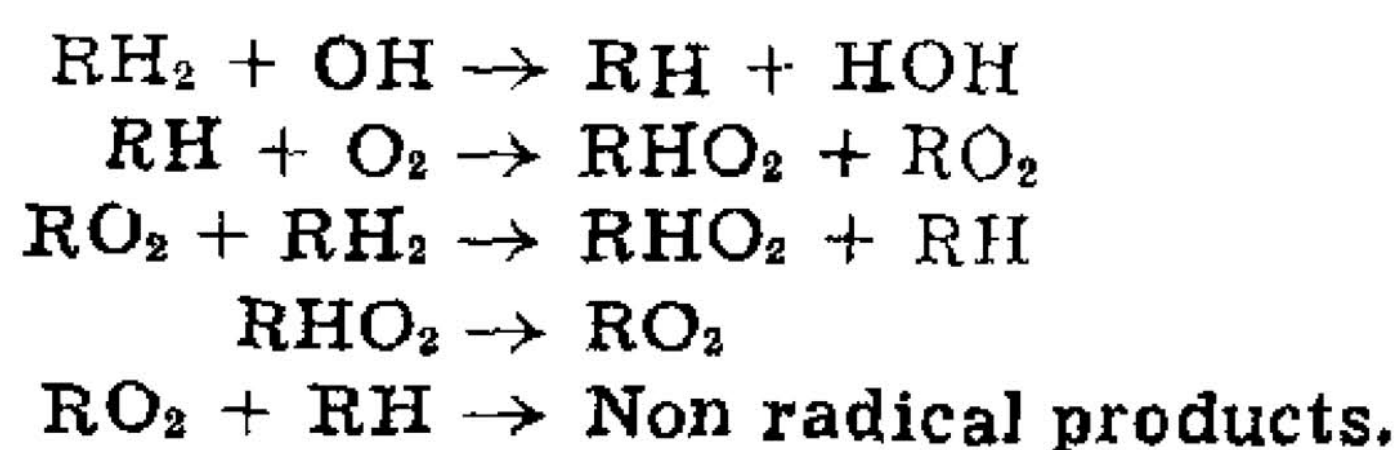
$$\ddot{N}=\overset{+}{N}=\overset{..}{\overset{..}{N}}: \;\; ; \;\; \overset{..}{N}-\overset{+}{N}\equiv N: \;\; ; : \;\; \overset{+}{N}\equiv N-\overset{..}{N}: \; .$$
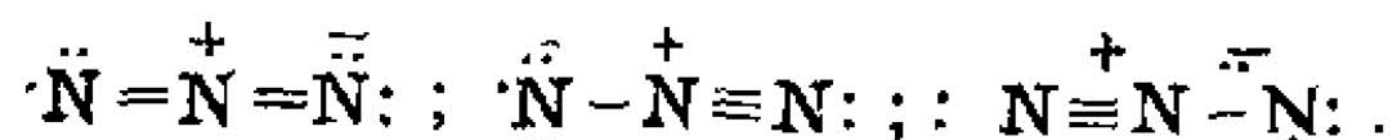
In the absence of monomer, hydroxyl or chloride radicals might be removed from the system by their reaction with impurities, say RH_2,

$$RH_2 + OH \longrightarrow RH + HOH$$
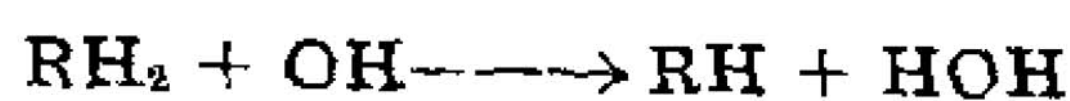
The radicals (RH) formed from impurities may involve in oxidative reactions by either (i) electron transfer reactions, $RH + Fe^{+2} \rightarrow RH^- + Fe^{+3}$ or (ii) abstraction of hydrogen atoms as indicated for OH radicals above. If electron affinity of the radical RH is high enough, electron transfer oxidation will be preferred whilst a high ionic bond dissociation energy for RH. H favours the oxidation by abstraction of hydrogen atom. If the radicals formed from impurities and those produced from the ion-pair complex are of the same order of electron affinity, then there will be same heat change and equal extents of their reaction with ferrous ion. On the other hand, if the bond dissociation energy OH. H is much greater than RH...H then the following reaction occurs:

$$RHH + OH \rightarrow HOH + RH$$

and the difference in the bond dissociation energies is reflected in the exothermicity of the reaction. Another possible way of removal of OH radicals from the system may involve trace of oxygen;

$$RH_2 + OH \rightarrow RH + HOH$$
$$RH + O_2 \rightarrow RHO_2 + RO_2$$
$$RO_2 + RH_2 \rightarrow RHO_2 + RH$$
$$RHO_2 \rightarrow RO_2$$
$$RO_2 + RH \rightarrow \text{Non radical products.}$$

Yet a third possibility of reactions of radicals from impurities may be conceived as represented by the following steps:

$$RH + Fe^{+3} \rightarrow RH^+ + Fe^{+2}$$
$$RH + Fe^{+3}OH^- \rightarrow HROH + Fe^{+2}$$
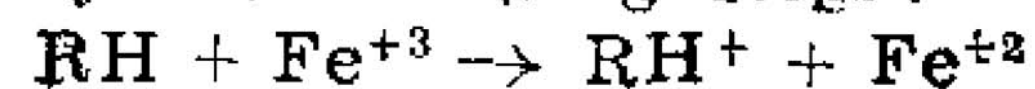
Whether the hydroxyl or chloride radicals would give rise to radicals which would photosensitize illuminated ferric salts and photodecompose water at the intensities used, it is not possible to say with certainty though this might be a useful field for investigation.

Many more possible ways of inter-reactions of radicals and ions obtaining in the system might be proposed depending upon the type of impurity present. A fruitful field in this direction is to get quantitative data on the nature of impurities, the electron affinities of radicals and the ionic bond dissociation energies of the impurities present before more light can be thrown on the reactivities of radicals towards impurities in aqueous solution.

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