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Notes

Effect of food dyes on radicals in aqueous media

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Abstract

The rates of reaction of photogenerated hydroperoxy and hydroxyl radicals on the photostability of aqueous solutions of dequalinium chloride irradiated with simulated sunlight at 38 ± 1°C have been investigated, with and without the addition of amaranth and quinoline yellow. These reactions follow second-order kinetics and the dyes tested markedly increase the rate constants of the reactions. Hydroperoxy radicals react with hydroxyl radicals preferentially to the dequalinium chloride resulting in lower reaction rate constants for the latter. Acetaldehyde was used as a scavenger of hydroperoxy radicals.

Keywords: Amaranth (E123); 2,2′-Azobis(2-amidinopropane) dihydrochloride (ABAP); Dequalinium chloride; Quinoline yellow (E104); Hydrogen peroxide; Hydroxyl radical; Hydroperoxy radical; Photodegradation

Dequalinium chloride was used as a model compound to study the effects of food dyes as potentiators of photochemical degradation of pharmaceutical products mediated by hydroxyl and hydroperoxy radicals. Patel and Sugden (1992) showed that dequalinium chloride undergoes photodegradation on irradiation with simulated sunlight in the presence of hydrogen peroxide, the reaction being mediated by hydroxyl radicals. Czapski (1972) demonstrated that photolysis of water can yield both hydroxyl and hydroperoxy radicals. Niki et al. (1988) showed that 2,2′-azobis(2-amidinopropane) dihydrochloride (ABAP) would generate hydroperoxy radicals in aqueous solutions. Food dyes are used in medicinal preparations to enhance their acceptability but dyes are known to facilitate photodegradation by charge transfer (Suppan, 1972) and to undergo decomposition (Koval'chuk et al., 1986). The objective of this work is to investigate the rates of photodegradation of the model system by hydroxyl and hydroperoxy radicals at 38 ± 1°C.

The following materials were obtained from the indicated sources: 2,2′-azobis(2-amidinopropane) dihydrochloride (ABAP) (Polyscience Inc., USA), dequalinium chloride (Sigma Chemical Co.), amaranth (E123) (BDH), quinoline yellow (E104) (Aldrich Chemical Co.) and hydrogen peroxide (30%) (Boots plc)

A Beckman DU 70 UV/visible spectrophotometer with matched silica cells (1 cm path length) was used.

A calibration curve was constructed from means of eight readings for each point for dequalinium chloride in deionised water using a

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Table 1

Irradiation of dequalinium chloride with ABAP in deionised water

Time (h)	Absorbance at 326 nm	% DC[a] remaining	Log % DC[a] remaining	1/% DC[a] remaining
0	0.888	100.00	2.0000	0.01000
7	0.860	96.85	1.9861	0.01032
24	0.761	85.69	1.9329	0.01167
31	0.756	85.14	1.9301	0.01174
48	0.712	80.18	1.9041	0.01247
55	0.645	72.64	1.8611	0.01377
72	0.633	71.28	1.8529	0.01403
79	0.587	66.10	1.8202	0.01513
96	0.582	65.54	1.9165	0.01526
102	0.537	60.47	1.7816	0.01654
167	0.350	39.41	1.5957	0.02537
	regression (r) coefficients	-0.989	-0.989 slope = 0.00229 rate constant = 5.27×10^{-3}	0.876

[a] DC, dequalinium chloride.

concentration range of 0.1–0.8 mg/l which obeyed the Beer Lambert Law (regression coefficient, -0.9996. $p = 0.001$). Solutions of dequalinium chloride (10 mg/l) were prepared in deionised water, hydrogen peroxide was added (0.5% v/v). A series of solutions containing dyes were prepared as above with the addition of the dye (0.2 μg/200 ml). A series of solutions with ABAP were prepared containing 1.02 mg/100 ml with and without hydrogen peroxide, and the dyes tested. All the solutions were irradiated according to the method of Evans et al. (1975) and the dequalinium chloride content assayed by UV spectroscopy and the results treated using the method of Patel and Sugden (1992).

The experimental results are listed in Tables 1 and 2. Table 2 shows that the photodegradation of dequalinium chloride solution and hydrogen peroxide on irradiation with simulated sunlight follows first-order kinetics, as reported by Patel and Sugden (1992). The addition of the two dyes tested produces a change in reaction order from first to second order. Irradiation of dequalinium chloride solution with added ABAP gave a rate constant of 0.08×10^{-3}. Incorporation of the two food dyes gave rate constants of 8.28×10^{-3} and

Table 2

Summary of the photodegradation of aqueous solutions of dequalinium chloride with additives

Solution with additive	Order of reaction	Mean rate constant
DC + H_2O_2	first	31.45×10^{-2}
DC + H_2O_2 + amaranth	second	5.86×10^{-3}
DC + H_2O_2 + quinoline yellow	second	4.22×10^{-3}
DC + ABAP	second	0.08×10^{-3}
DC + ABAP + amaranth	second	8.28×10^{-3}
DC + ABAP + quinoline yellow	second	8.69×10^{-3}
DC + ABAP + amaranth + H_2O_2	second	6.82×10^{-3}
DC + ABAP + quinoline yellow + H_2O_2	second	6.90×10^{-3}
DC + ABAP in dark	–	no reaction
DC + ABAP + amaranth + acetaldehyde	–	no reaction
DC + ABAP + quinoline yellow + acetaldehyde	–	no reaction

DC, dequalinium chloride; ABAP, 2,2′-azobis(2-amidinopropane) dihydrochloride.

8.69×10^{-3} with amaranth and quinoline yellow respectively. ABAP and dequalinium chloride did not react in the dark, indicating that light was needed to form hydroperoxy radicals from ABAP. The differences between the rate constants for the control (Table 1) and the solutions containing the test dyes suggested that the dyes promoted the photodegradation of dequalinium chloride by hydroperoxy radicals.

Methylene blue is reported to photo-oxidise water in acid solution to hydrogen peroxide by a two-photon process, the yield of leuco methylene blue being greater than 10^{-3} in red light (Bryce-Smith, 1975). This suggests that the energy requirement for this reaction is low enough for sunlight or strip-light to provide the energy needed. However, the pH of the solutions irradiated in the present work was not controlled, as this action would have introduced an artificial constraint with respect to products. Irradiation of both of the two dyes with dequalinium chloride, ABAP and acetaldehyde showed absence of photodegradation of the dequalinium chloride, indicating that acetaldehyde was acting as a powerful scavenger of the hydroperoxy radical, as suggested by Kochi (1973). Irradiation of a solution of dequalinium chloride with ABAP and hydrogen peroxide with amaranth incorporated followed second-order kinetics and gave a rate constant of 6.82×10^{-3}. A similar reaction with quinoline yellow also followed second-order kinetics and gave a rate constant of 6.90×10^{-3}. Both of these reactions had lower rate constants than those of the corresponding experiments without the addition of hydrogen peroxide. This suggested that the hydroxyl radicals formed from the hydrogen peroxide were reacting preferentially with the hydroperoxy radicals formed from the ABAP rather than reacting with the dequalinium chloride, supporting earlier reports (Hochanadel et al., 1980; Kurylo et al., 1981; Sridharan et al., 1981).

The hydroperoxy radical gives rise to higher rate constants than does the hydroxyl radical under the conditions of measurement, suggesting that hydroperoxy radicals present a threat to the stability of coloured formulations. Czapski (1972) reported that hydroperoxy radicals can be formed in any aqueous system in which oxygen is present, this is fulfilled in most aqueous products. Acetaldehyde has been used in the present work solely as a model hydroperoxy radical scavenger.

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