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ORIGINAL PAPER

C.A.C. Coiffard · L.J.M. Coiffard
Y.M.R. De Roeck-Holtzhauer

Photodegradation kinetics of acesulfame-K solutions under UV light: effect of pH

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Abstract The objective of this research was to study the effect of pH on the photodegradation of aqueous solutions of 5×10^{-5} M acesulfame-K (λ_{max}, 226 nm; ε, 11400 mol^{-1} L cm^{-1}). Photodegradation followed first-order kinetics and was found to be pH-dependent. The degradation rate constant was calculated to be 6.7×10^{-2} min^{-1}, 4.5×10^{-2} min^{-1}, 3.4×10^{-2} min^{-1} and 17.4×10^{-2} min^{-1}, respectively, at pH 3, pH 9 and pH 12.

Key words Photodegradation · Acesulfame-K · Aqueous diluted solutions · pH

Introduction

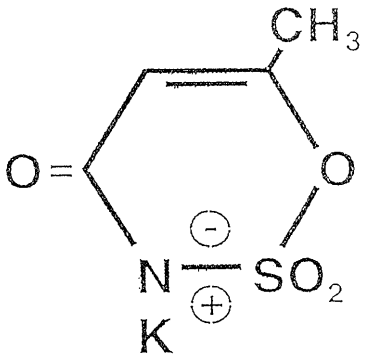
Acesulfame-K was first synthesis by Clauss and Jensen (Hoechst, Frankfurt) in 1967. Acesulfame-K is rapidly absorbed by the intestine and is found unchanged in the urine because it is not metabolised [1, 2]. Thus, it does not accumulate in organisms [3]. Acesulfame-K, which stimulates the release of insulin [4] can be utilised by diabetics because it does not interfere with glucidic metabolism. The flavour of acesulfame-K and cyclamate is comparable [5]. Acesulfame-K is 200 times sweeter than sucrose. It is characterised by a total lack of aftertaste [6–9] and associated side-effects [10–12]. Previous studies have established that acesulfame-K is extremely thermostable with in a wide pH range (from 2.5 to 9) [13, 14]. To complete our knowledge of the stability of this sweetener we carried out a study to determine the photostability of acesulfame-K, as no data have been previously published on the photodegradation of this sweetener.

C.A.C. Coiffard · L.J.M. Coiffard (✉)
Y.M.R. De Roeck-Holtzhauer
Laboratory of Industrial Pharmacy, School of Pharmacy,
University of Nantes, 1 Rue Gaston Veil,
F-44035 Nantes Cedex, France

Materials and methods

Materials. Acesulfame-K [the K salt of 3,4-dihydro-6-methyl-1,2,3-oxathiazine-4-one 2,2-dioxide (tradename: "Sunett", Hoechst, Germany); (Fig. 1), a white odourless powder, was obtained from Hoechst (batch no. 701 NAA 066). All chemicals used were of analytical quality. Distilled H_2O was obtained from an Autostill 4000X (Jencons).

Experimental protocol. Solutions of acesulfame-K (5×10^{-5} M at various pH) were enclosed in spectrophotometer tubes and exposed to the light source in a light-stability cabinet (Original Hanau Quartzlampen). The intensity of UV-A and UV-B was measured with an Osram apparatus (Centra-UV-Meßgerät). The intensity of UV-A was maintained at 6.45 mW cm^{-2} and that of UV-B at 1.47 mW cm^{-2}. All tubes containing acesulfame-K solutions were covered with Al foil before exposure to UV light in order to eliminate the influence of heat generated by the light within the cabinet. The pH of these solutions was adjusted to the desired values with 0.01 M HCl, 0.333 M H_3BO_3, 0.970 M H_3BO_3, 3.23×10^{-5} M $Na_2B_4O_7$, 0.02 M $Na_2B_4O_7$ and 0.075 M NaOH. The pH of these solutions were determined with a Metrohm Herisau pH meter, model E300B, equipped with a Refill Ingold I



potassium salt of 3,4 - dihydro - 6 - methyl - 1,2,3 - oxathiazine - 4 - one 2,2 - dioxide

$C_4H_4O_4SNK$ ε_{max} = 11400 mol^{-1} L cm^{-1}

Molecular weight : 201.243 U.V. (water) λ_{max} = 226 nm

Fig. 1 Chemical structure of acesulfame-K, λ_{max} and ε values

3556 (pH = 0–14, temperature 0–80 °C) electrode which was standardised with panreac solutions at pH 4 and pH 10. Measurements were carried out at 20 °C.

Absorbance spectrum and analysis of acesulfame-K. The absorbance spectrum of acesulfame-K was analysed between 200 and 400 nm with a spectrophotometric method (Hitachi UV-visible double-beam spectrophotometer, model U-2000). A liquid chromatographic method was utilised for the determination of the acesulfame-K concentrations, initially and at various times. HPLC was carried out with a system consisting of a Waters model 655 A-12 pump, a Waters Lambda Max model 481 LC variable-wave length detector set at 226 nm and a Merck D-2500 model integrator controlled with a L-5000 LC controller (Hitachi). Each solution was analysed under the following conditions: reversed-phase analytical column (300 × 3.9 mm packed with 10-μm μBondapack-C_{18} waters); volume injected, 10 μl; temperature, 20 °C ; flow rate, 0.8 ml min^{-1}; detector attenuation, 0.2 AUFS. The mobile, phase was 0.0125 M KH_2PO_4 (pH 3.5)/acetonitrile (90/10). The pH of the buffer was adjusted to 3.5 with 5% phosphoric acid. The buffer and acetonitrile were separately filtered through a 0.45-μm filter (Millipore), mixed in the desired proportions and degassed. The analyses were carried out in triplicate and the difference between the triplicates was $<1\%$.

Analysis of variance and least significant differences ($P<0.05$) were computed from the results.

Table 1 Composition of buffer salts added to acesulfame-K and pH of final solutions

Buffer type	Concentration (M)	pH
None	–	6
H_3BO_3	0.970	3
$Na_2B_4O_7$	0.020	9
NaOH	0.075	12

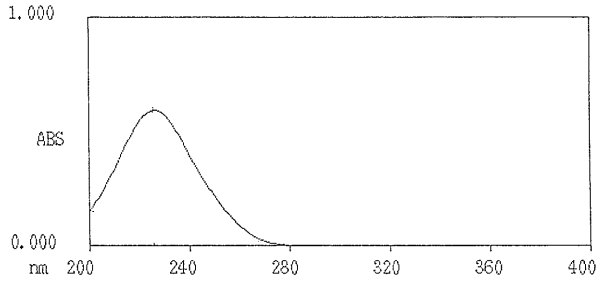


Fig. 2 UV spectrum of 5×10^{-5} M acesulfame-K in aqueous solution. *ABS* absorbance

Results and discussion

Kinetics of acesulfame-K degradation

The pH of different solutions are given in Table 1. The spectrum of acesulfame-K showed maxima at 226 nm (Fig. 2).

Each solution was injected on the HPLC where the area of the peaks at 226 nm were measured. A linear relationship was found between area of the peak and concentration for the range of concentrations analysed (5–15 mg l^{-1}; $r=0.9999$).

The photodegradation of acesulfame-K was expressed as the rate of change in peak area of the peak detected at 7 min. We observed a gradual decrease in the peak area during photolysis. The degradation rate constant was calculated from the slope of the line of peak area (7 min) versus time. The percentage of substance remaining was calculated. The photodegradation of acesulfame-K in aqueous solution (Fig. 3) followed first-order kinetics and is described by the following equation:

$$C/C_0 = e^{-k_a t} \quad (1)$$

where C and C_0, are the concentrations of acesulfame-K at time t and $t=\phi$, respectively, and k_a is the first-order degradation rate constant. The degradation rate constant, was calculated to be 4.5×10^{-2} min^{-1}.

Effect of pH

The photodegradation of 5×10^{-5} M acesulfame-K in buffer solution at a pH of 3, 9 and 12 was studied. The

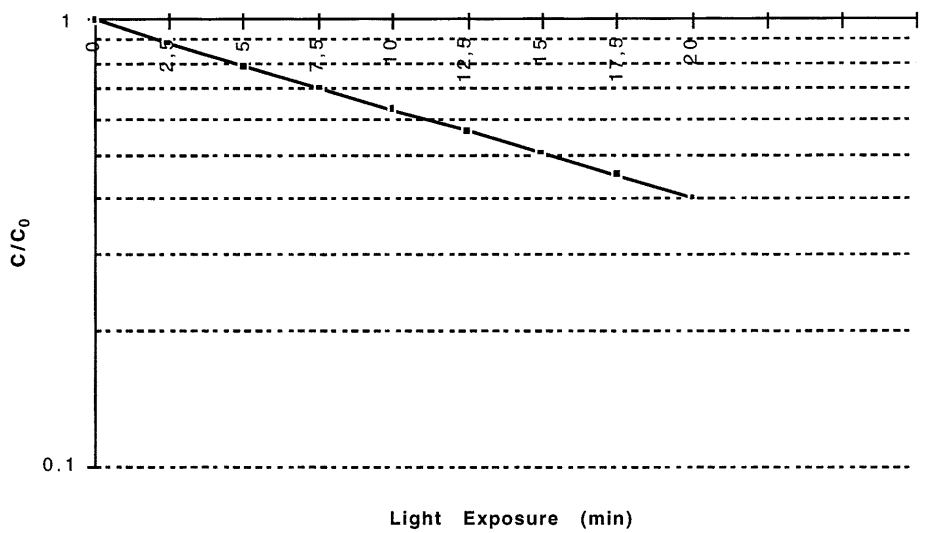


Fig. 3 Kinetics of the photodegradation of an aqueous solution of 5×10^{-5} M acesulfame-K at pH 6. Data are the means of three measurements. C concentration of acesulfame-K at time t; C_0 concentration of acesulfame-K at $t=\phi$

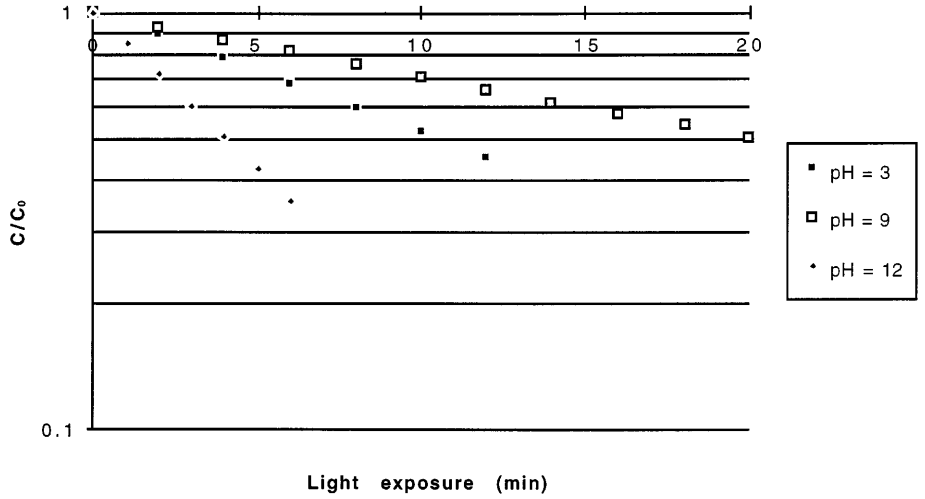


Fig. 4 Kinetics of the photodegradation of 5×10^{-5} M acesulfame-K at various pH. Data are the means of three measurements. For abbreviations, see Fig. 3

Table 2 Photodegradation of aqueous solutions of acesulfame-K. *C* concentration of acesulfame-K at time *t*; C_0 concentration of acesulfame-K at $t=\phi$

Times (min)	C/C_0			
	pH 3	pH 6	pH 9	pH 12
0	1.000	1.000	1.000	1.000
1	–	–	–	0.850
2	0.890	0.903	0.923	0.714
3	–	–	–	0.600
4	0.778	0.825	0.862	0.504
5	–	–	–	0.423
6	0.680	0.753	0.805	0.355
7	–	–	–	–
8	0.595	0.688	0.752	–
9	–	–	–	–
10	0.520	0.629	0.702	–
11	–	–	–	–
12	0.455	0.574	0.656	–
13	–	–	–	–
14	–	0.525	0.613	–
15	–	–	–	–
16	–	0.479	0.572	–
17	–	–	–	–
18	–	–	0.534	–
19	–	–	–	–
20	–	–	0.499	–

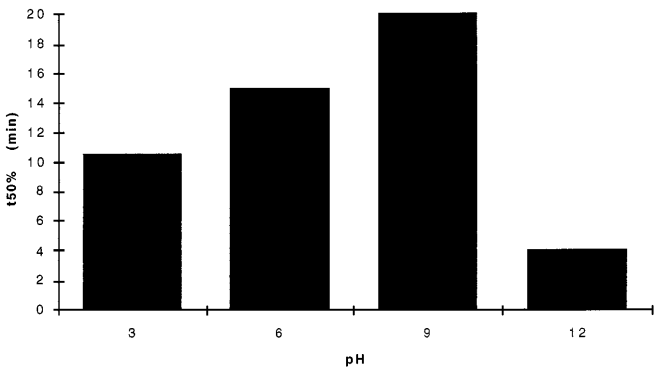


Fig. 5 Half-lives (*t 50%*, min) of 5×10^{-5} M acesulfame-K solutions at various pH. *Bars* are significantly different from each other at $P<0.05$

Table 3 Degradation rate constants (*k*) of 5×10^{-5} M acesulfame-K solutions at various pH. *SEM* Standard error of means ($n=3$)

pH	k (min^{-1}) ± SEM
3	$6.7\times10^{-2}\pm0.54\times10^{-2}$
6	$4.5\times10^{-2}\pm0.23\times10^{-2}$
9	$3.4\times10^{-2}\pm0.15\times10^{-2}$
12	$17.4\pm10^{-2}\pm1.50\times10^{-2}$

[a] Significantly different ($P<0.05$) relative to pH

chromatograms obtained during photolysis demonstrated a gradual decrease in the area of the peak detected at 7 min. The degradation rate constant was calculated from the slope of peak area versus time. The percentage of acesulfame-K remaining was calculated at various pH values (Table 2). Whatever the pH, the photodegradation of acesulfame-K in diluted buffer solutions followed first-order kinetics (Fig. 4) and was described by the following equation:

$$C/C_0=e^{-k_b t} \quad (2)$$

where k_b is the apparent first-order degradation rate constant. At a pH of 3, 9 and 12, we noted a variation in the values of the rate constant k_b (see Table 3). The pH of the solution influenced the photostability of acesulfame-K. This relationship between pH and photostability has been found for many organic molecules [15]. The effect of pH on the shelf-life of acesulfame-K is significant at pH values of 3 and 12 (Fig. 5). The percentage increase in the stability of acesulfame-K by the addition by buffer was found to be 43% and 33% between pH 3 and 6 and pH 6 and 9, respectively.

The present study has completed our knowledge of the stability of acesulfame-K. This molecule appears to be very photodegradable and extremely thermostable [13]. We have established the best pH storage conditions for acesulfame-K, which are the following: a medium with a pH of 6 to 9. In order to avoid the photodegradation of acesulfame-K, packing materials of pro-

cessed food containing this compound should totally absorb UV radiation.

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