

Hydrothermal stability of the new sweetener *acesulfame K*

MILAN SUHAJ — MILAN KOVÁČ — MICHAL UHER — TERÉZIA VACOVÁ

Summary. A procedure for laboratory synthesis of the new sweetener *acesulfame K* has been worked out. The stability of the compound in solutions has been studied at 100°C in dependence on the initial concentration of the product and pH value of the media, based on concentration measurements in UV region. The half-life values were calculated. *Acesulfame K* decomposition was found to follow a first order reaction and the decomposition rate constants were calculated. The results indicate that, under the experimental conditions, *acesulfame K* is relatively stable, the solutions being most stable in the pH region 5 to 7. Lower pH values contributed to faster *acesulfame K* decomposition. The fastest decomposition of *acesulfame K* in a solution was observed in alkaline region. In spite of the observed relatively good stability of *acesulfame K* under the assumed conditions of its technological use, further attention will be devoted to more detailed study of its optimum utilization with respect to the protection of consumers' health.

Future development of food industry is directly bound to intensive utilization of food additives, among which synthetic sweeteners have an important place. In CSSR, the production of Usal as a further synthetic sweetener has been started, to complement the still used saccharin and cyclamates. A new sweetener *acesulfame potassium* seems to be promising for perspective use. It is currently being evaluated within the FAO/WHO framework.

Acesulfame K is 6-methyl-1,2,3-oxathiazin-4(3H)-one-2, 2-dioxide potassium salt. It had been discovered in 1967 and testing of its hygienic acceptability and technological evaluation are in progress ever since. *Acesulfame K* is a white crystalline powder, odourless, with an intensively sweet taste. It is well soluble

Ing. Milan Suhaj, Ing. Milan Kováč, CSc., Ing. Terézia Vacová, CSc., Food Research Institute, Trenčianska 53, 825 09 Bratislava.

Assoc. Prof. Ing. Michal Uher, CSc., Department of Chemistry and Technology, of saccharides and Food-stuffs, Faculty of Chemical Technology, Slovak Technical University, Jánska 1, 812 37 Bratislava.

in water, less soluble in ethanol. Acesulfame K is about 200 times sweeter than sucrose, the relative intensity of sweetness being higher at lower concentrations. At higher concentrations of acesulfame K in solution, the sweetness drops down to 100—130 — fold compared to sucrose. The sweet taste is perceived immediately at consumption and is more persistent than that of sucrose but it is free of unpleasant off-flavour. In solid state, *acesulfame K* is highly stable and it is not hygroscopic. It is decomposed at about 225°C [1, 2].

The metabolic studies done until now showed acesulfame K is not metabolized in the organism, it is readily excreted from the organism unchanged, its energetic value thus being practically zero. It is resistant to the digestive tract bacteria. Neither bactericidal nor promotoric effect has been observed. No induced degradation of bacteria strains has been proved even after prolonged action. No induced metabolism has been observed in rats after extended *acesulfame K* action followed by¹⁴ C-acesulfame K application. Except for the effect of potassium, *acesulfame K* has no pharmacological effect [2].

In Codex Alimentarius, specifications have been worked out for *acesulfame K* with respect to the evaluation of identity confirmation and evaluation of purity. Acesulfame K must not contain more than 3 mg.kg⁻¹ arsenic, 30 mg.kg⁻¹ selenium, 30 mg.kg⁻¹ fluorides, and the total content of heavy metals must not exceed 10 mg.kg⁻¹. The list of acceptable acesulfame K additives for the individual foodstuffs has so far not been prepared by FAO/WHO, however, the ADI value has been determined in the range of 0 to 9 mg.kg⁻¹ of body weight [3, 4].

In Great Britain and Ireland, FRG and Belgium, acesulfame K has been already approved for foodstuffs use and is marketed under the name Sunett. It is expected that further countries obtain consent for its application in near future.

Acesulfame K is economically more advantageous than Usal and many other sweeteners. From the price comparison on American market it follows that the price of this new sweetener per sweetening unit is about 3,5 times lower compared to beet sugar and it is close to the prices of the most widely used synthetic sweeteners saccharin and cyclamates.

Analogically to other synthetic sweeteners, the largest field for the possible application of *acesulfame K* are soft drinks where the product may be used both in dry form and as stock solution. Its use is also anticipated for sweetening beer, wine and spirits. In case of application into other foods, where sugar has also other functions apart from the sweet taste (the required volume of the products, taste, flavour and colour resulting from Maillard reactions, preserving effect due to the increased osmotic pressure etc.), the substitution of sugar should be solved by combining acesulfame K with hydrocolloids and other additives. *Acesulfame K* is expected to find use as sweetener in bakery and confectionary

products, fruit spreads, chewing gums, and in the production of mouth cosmetics.

The studies of the application areas abroad concentrate mainly on the relations between the concentration of acesulfame K and sweetness as well as on influencing the taste by synergic effect of acesulfame K with other sweeteners. The results are mainly patents for preparation of sweetener mixtures used for low-energy products such as combinations of acesulfame K with fructose [5], saccharin [6] or other sweeteners.

The problem of thermal and hydrolytic stability of acesulfame K is important from both technological and hygienic aspect, as background information for the determination of suitable application conditions and stability of the final product.

The German manufacturer (Hoechst A. G.) states that *acesulfame K* is stable for several months at the temperatures below 40°C and pH 3 to 8. The hydrolysis yielding mainly acetone and CO₂ (by decomposition of acetylacetic acid) takes place under extreme conditions, at pH below 2,5 or in strongly alkaline solutions. It is also stated that *acesulfame K* water solutions can be sterilized and stored for one month without hydrolysis [7]. Increased attention should be paid to acesulfame K stability as the basic condition for ensuring the health innocuousness of foods where this new sweetener is proposed for use.

Materials and Methods

The new sweetener *acesulfame K* was synthesized under laboratory conditions according to the procedure worked out by the workers of the Chair of organic chemistry of Slovak Technical University. Chlorsulphonylisocyanate used as the starting material was reacted with 3-oxobutyric acid tertiary butyl ester to yield acesulfame K (Fig. 1).

The structure of the product was confirmed by IR and ¹H NMR spectra. The UV spectrum of the synthesized *acesulfame K* in neutral medium was found to comply with the FAO identification test, i. e. the product had an absorption maximum at 227 ± 2 nm [3]. Out of the neutral pH region a shift of the absorption maximum was observed.

Acesulfame K solutions were prepared in the concentration range of 0,05 to 1,00 g.l⁻¹, at pH values ranging from 3 to 11. The pH value of the medium was adjusted using compounds not interfering in the solutions with the UV-spectra measurements. All buffer solutions for pH adjustment were prepared so that their ionic strength was I = 0,1 under the following conditions:

Results and Discussion

The absorption spectra of *acesulfame K* in UV region and its changes at hydrothermal degradation are shown in Fig. 2.

The study of hydrothermal stability of *acesulfame K* at 100°C showed a considerable influence of the pH value of the medium. Results of *acesulfame K* determinations in dependence on the initial concentration and time at different pH values are given in Tables 1 through 5. The Tables also give the values of half-lives and rate constants separately for each concentration. The concentration changes of *acesulfame K* in dependence on time and pH at 100°C are illustrated in Fig. 3.

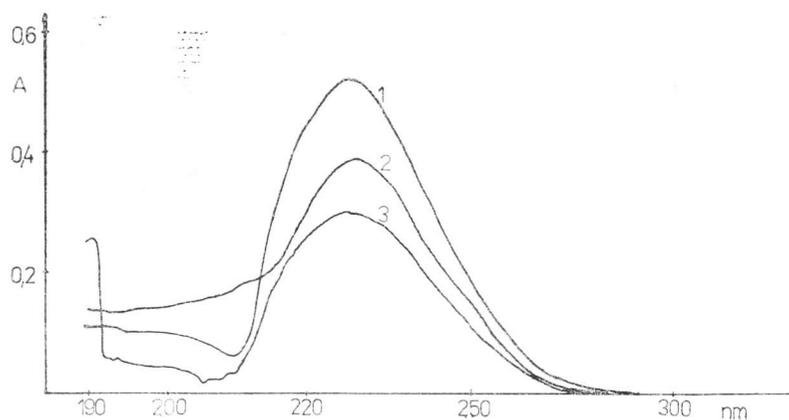


Fig. 2. Absorption spectra of *acesulfame K* solution ($0,01 \text{ g.l}^{-1}$) at $\text{pH} = 5$

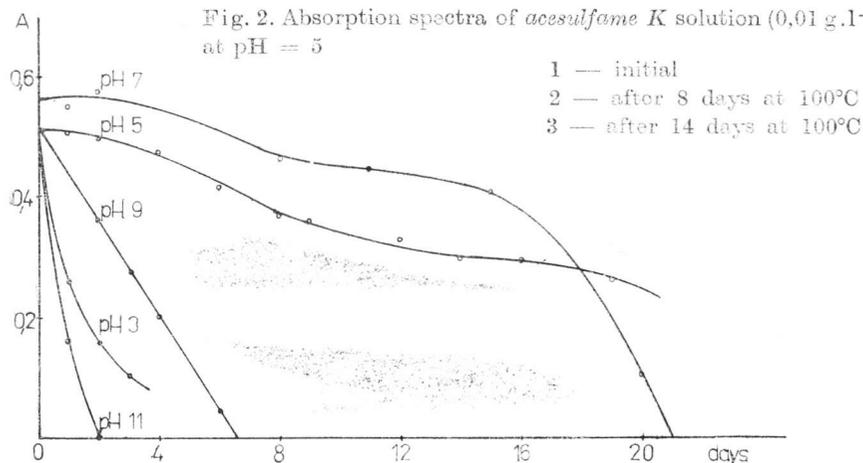


Fig. 3. Changes in the absorbance of *acesulfame K* solutions ($0,01 \text{ g.l}^{-1}$) maintained at 100°C and different pH values in dependence on time

Table 1. Hydrothermal degradation of *acesulfame K* at 100°C and pH 3

Time (days)	<i>Acesulfame K</i> concentrations (g.l ⁻¹)			
0	0,050	0,100	0,500	1,000
1	0,025	0,043	0,233	0,458
2	0,015	0,025	0,133	0,295
3	0,010	0,015	0,083	0,095
τ (h) k (h ⁻¹)	24,0 2,88 · 10 ⁻²	18,0 3,85 · 10 ⁻²	21,1 3,28 · 10 ⁻²	21,1 3,28 · 10 ⁻²

Table 2. Hydrothermal degradation of *acesulfame K* at 100 °C and pH 5

Time (days)	<i>Acesulfame K</i> concentrations (g.l ⁻¹)			
0	0,050	0,100	0,500	1,000
1	0,049	0,098	0,488	0,965
2	0,048	0,096	0,491	0,979
4	0,046	0,093	0,469	0,939
6	0,040	0,078	0,396	0,842
8	0,036	0,076	0,383	0,797
9	0,035	0,074	0,364	0,769
12	0,032	0,067	0,334	0,682
14	0,029	0,060	0,295	0,647
16	0,028	0,058	0,298	0,624
19	0,026	0,258	0,258	0,494
τ (h) k (h ⁻¹)	484,8 1,43 · 10 ⁻³	492,0 1,41 · 10 ⁻³	492,0 1,41 · 10 ⁻³	468,0 1,48 · 10 ⁻³

As can be seen from the calculated half-life values of *acesulfame K* decomposition, these values are similar at the same pH values. Thus, at a given pH value and constant temperature, the rate of decomposition of the product does not depend on its initial concentration and the hydrothermal decomposition of *acesulfame K* can be considered a first-order reaction. This is also evidenced by the calculated reaction order with values between 0 and 1.

The stability of *acesulfame K* and its decomposition rate at 100°C and the pH values given can be evaluated by the rate constants calculated from the equation for first order reactions:

$$k = \ln 2 \cdot \tau^{-1} [9]$$

Table 3. Hydrothermal degradation of *acesulfame K* at 100 °C and pH 7

Time (days)	<i>Acesulfame K</i> concentrations (g.l ⁻¹)				
0	0,05	0,100	0,500	1,000	5,000
1	0,049	0,099	0,496	0,990	4,965
2	0,049	0,098	0,488	0,981	4,959
4	0,048	0,094	0,488	0,966	4,824
5	0,047	0,090	0,469	0,945	4,715
8	0,041	0,084	0,414	0,780	3,977
11	0,040	0,074	0,418	0,713	4,067
15	0,036	0,069	0,363	0,489	3,067
18	0,024	0,021	0,251	0,225	1,484
20	0,009	0,001	0,118	0	0,038
21	0,002	0	0,029	0	0
τ (h)	428,4	352,8	432,0	355,2	388,8
k (h ⁻¹)	$1,62 \cdot 10^{-3}$	$1,96 \cdot 10^{-3}$	$1,60 \cdot 10^{-3}$	$1,95 \cdot 10^{-3}$	$1,78 \cdot 10^{-1}$

Table 4. Hydrothermal degradation of *acesulfame K* at 100°C and pH 9

(days Time)	<i>Acesulfame</i> concentrations (g.l ⁻¹)			
0	0,050	0,100	0,500	1,000
1	0,044	0,088	0,444	0,841
2	0,037	0,074	0,371	0,719
3	0,028	0,059	0,305	0,588
4	0,020	0,043	0,238	0,442
6	0,004	0,014	0,098	0,167
τ (h)	79,2	84,0	92,2	85,2
k (h ⁻¹)	$8,75 \cdot 10^{-3}$	$8,25 \cdot 10^{-3}$	$7,59 \cdot 10^{-3}$	$8,13 \cdot 10^{-3}$

The decomposition rate of *acesulfame K* at 100°C characterized by changes in the pH values of the solutions and by rate constant values is different at different pH of the initial buffer solutions. The degradation is obviously the slowest in weakly acidic solution at pH 5 where rate constants from $1,41 \cdot 10^{-3}$ to $1,48 \cdot 10^{-3} \text{ h}^{-1}$ were determined. Increasing pH of the medium results in faster decomposition of *acesulfame K*. This can be concluded from the rate constants values which are approximately 5 times higher at pH 9 in comparison with the values obtained at pH 7 ($7,6 \cdot 10^{-3}$ to $8,8 \cdot 10^{-3} \text{ h}^{-1}$). The fastest decomposition of *acesulfame K* was observed at pH 11 where the rate constants were as high as $4,8$ to $5,3 \cdot 10^{-2} \text{ h}^{-1}$. Analogically, the pH shift towards strongly acidic region resulted in faster decomposition of the product compared with the decom-

Table 5. Hydrothermal degradation of *acesulfame K* at 100°C and pH 11

Time (days)	<i>Acesulfame K</i> concentrations (g.l ⁻¹)			
0	0,050	0,100	0,500	1,000
1	0,014	0,031	0,159	0,346
2	0,002	0,006	0,062	0,154
3	0	0	0,032	0,110
τ (h)	13,2	14,4	14,4	14,4
k (h ⁻¹)	5,25 · 10 ⁻²	4,81 · 10 ⁻²	4,81 · 10 ⁻²	4,81 · 10 ⁻²

position rate in neutral medium. The decomposition in acidic medium is, however, slower than that in alkaline medium. At the pH value of 3 which had been chosen as an extreme value for very acidic foods the decomposition rate of *acesulfame K* was characterized by rate constants values between $2,9 \cdot 10^{-2}$ and $3,9 \cdot 10^{-2} \text{ h}^{-1}$.

With respect to its high sweetening ability *acesulfame K* may be expected to be practically used at low concentrations. The product would be subjected to the 100°C temperature considered throughout this study only for a limited time (cooking or sterilization of the foods). The anticipated application region is within neutral or acidic pH higher than pH = 3. The results presented here show that the decomposition rate of *acesulfame K* at conditions considered for practical application is relatively low. At pH 7 and pH 5, the initial concentration of *acesulfame K* in the solution is practically maintained after 24 hrs at 100°C; at the extreme value of pH = 3 the final concentration is approximately one-half of the starting concentration.

As already stated, the decrease of *acesulfame K* concentration in the solution is not crucial from the technological aspect. However, further attention will pay to kinetic studies and identification of the decomposition products of *acesulfame K*, in order to characterize the stability of this new synthetic sweetener and find out the optimum conditions of its use in food industry in compliance with health protection standards.

References

1. LIPINSKI, G. W.: The future of *acesulfame K*. *Food Manuf.*, 58, 3, 1983, p. 51.
2. UHER, M. et al.: Prieskum syntézy niektorých syntetických sladidiel II. (Research report). Bratislava Faculty of Chemical Technology, Slovak Technical University 1985.
3. *Acesulfame Potassium*, FAO Food and Nutrition Paper 28, Specification for Identity and Purity, JECFA, Rome 1983.

4. Evaluation of certain food additives 25. Report of the Joint FAO/WHO Expert Committee on Food Additives, WHO Technical Report Series No. 669, Geneva 1982.
5. TORNOUT, P. — PELGROM, J., — MEEREN, J.: Sweetness evaluation of mixtures of fructose with saccharin, aspartame or *acesulfame K*. *J. Food Sci.*, 50, 1985, 2, 469—472.
6. ANON.: Low calorie sweeteners. *Food Engineering* 1983, 55, 5, 138—139.
7. ARPE, H. J.: *Acesulfame K* a new noncaloric sweetener. In: European Research Group for oral biology (20th symposium), 1979, 178—183.
8. DAVÍDEK, J. a kol.: Laboratorní příručka analýzy potravin. Praha SNTL, Alfa, 1981.
9. KELLÖ, V., TKÁČ, A.: Fyzikálna chémia Bratislava, Alfa 1969, p. 525—526.
10. Anon.: Problematika sladidiel. Informace o světovém potravinářství, sv. 7, 1984, p. 6.

Гидротермическая стабильность нового сладкого вещества Ацесульфам К

Резюме

Проведена разработка хода анализа нового сладкого вещества Ацесульфам К в лабораторных условиях и изучалась его стабильность в растворах при температуре 100°C в зависимости от исходной концентрации продукта и pH среды на основании измерений концентраций в ультрафиолетовой области. Проведены вычисления значений полу-периода разложения. Определено, что разложение Ацесульфам К протекает по реакции первого порядка и проведены вычисления констант скорости разложения. Результаты показали, что Ацесульфам К в наблюдаемых условиях относительно стабилен, причем растворы самые стабильные при pH 5—7. При низших значениях pH протекает разложение Ацесульфам К быстрее. Самое быстрое разложение изучаемого сладкого вещества протекает в растворе в щелочной области. Несмотря на то, что Ацесульфам К относительно стабилен при предполагаемых условиях его технологического применения, мы будем уделять внимание изучению его стабильности более подробно, чтобы были созданы условия для его оптимального применения с точки зрения безупречности пищевых продуктов.

Hydrotermická stabilita nového sladidla Acesulfamu K

Súhrn

Vypracoval sa postup syntézy nového sladidla *Acesulfamu K* v laboratórnych podmienkach a sledovala sa jeho stabilita v roztokoch pri 100 °C v závislosti od východiskovej koncentrácie produktu a pH prostredia, na základe meraní koncentrácií v UV oblasti. Vypočítali sa hodnoty polčasov rozkladu. Zistilo sa, že rozklad *Acesulfamu K* prebieha podľa reakcie prvého poriadku a vypočítali sa rýchlostné konštanty rozkladu. Výsledky dokázali, že *Acesulfam K* je pri sledovaných podmienkach pomerne stabilný, pričom najstabilnejšie roztoky sú pri pH 5—7. Pri nižších hodnotách pH prebieha rozklad *Acesulfamu K* rýchlejšie. Najrýchlejší rozklad sledovaného sladidla je v roztoku v alkalickéj oblasti. Napriek tomu, že *Acesulfam K* je pomerne dobre stabilný pri predpokladaných podmienkach jeho technologického uplatnenia, budeme venovať pozornosť štúdiu jeho stability podrobnejšie, aby sa vytvorili predpoklady pre jeho optimálne uplatnenie z hľadiska zdravotnej nezávadnosti potravinárskych výrobkov.