

Sonolysis of Aqueous 4-Nitrophenyl Acetate—No Evidence for Hydrolysis Induced by Transient Supercriticality

Armin Tauber, Heinz-Peter Schuchmann, and Clemens von Sonntag*^[a]

Abstract: The sonolysis of 4-nitrophenyl acetate in argon-saturated aqueous solution was studied at a frequency of 321 kHz. To examine the effect of OH radicals formed in the cavitation bubble and their reaction in the liquid phase with this substrate, a γ -radiolysis study was carried out as well. The OH radical adds preferentially in the *ortho* position to the ester function, thus forming 2-hydroxy-4-nitrophenyl acetate. Nitrite

and acetate are generated as minor products by *ipso* addition at the nitro and acetate substituents. Upon sonolysis, pyrolytic products (increased yields of nitrite, nitrate, gaseous products) are

also found. As 4-nitrophenol is not formed in the sonolysis of 4-nitrophenyl acetate, and as the acetate yield is largely accounted for by the OH-radical reactions occurring in the aqueous phase, the hydrolysis of 4-nitrophenyl acetate in the (transient) supercritical water layer inside the cavitation bubble can be ruled out as a pathway of its degradation.

Keywords: high-temperature chemistry • radical reactions • radiolysis • sonochemistry • supercritical fluids

Introduction

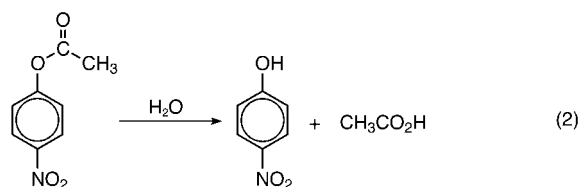
It is well-known that in liquids containing a dissolved gas, ultrasound can cause the formation of free radicals as a consequence of cavitation. It is generally accepted that these radicals are formed upon the collapse of the cavitation bubble, which can reach temperatures of several thousand degrees.^[1–7] In aqueous solutions, the decomposition of water vapor in the bubble leads to the formation of OH radicals and H atoms [Eq. (1)].^[8–11] Moreover, small amounts of O atoms



are formed in a sequence of subsequent reactions.^[12–14] A fraction of the radicals reach the aqueous phase where they either recombine or react with a solute. Additionally, a volatile solute can be drawn into the gas phase, where it may react with radicals and suffer pyrolysis.

The collapse of the bubble takes place within less than a microsecond. During the collapse phase, the hot cavitation bubble is surrounded by a zone^[15–17] that bears some resemblance to a thin layer of (transiently) supercritical water. Attempts have been made to monitor the appearance

of this domain by observing the sonolytic degradation of 4-nitrophenyl acetate^[18–20] or by following a decarboxylation reaction.^[21] The hydrolysis of 4-nitrophenyl acetate [Eq. (2)] is already detectable at room temperature in the absence of ultrasound; at a pH below 7 its specific rate is^[19] $6 \times 10^{-7} \text{ s}^{-1}$ ($8 \times 10^{-7} \text{ s}^{-1}$)^[22] and increases with increasing temperature ($E_a = 78 \text{ kJ mol}^{-1}$).^[19]



In these earlier reports,^[18–20] it was assumed that the sonolytic degradation of this ester is entirely due to hydrolysis in the supercritical water, and OH radical reactions or pyrolytic processes were not considered to contribute significantly to the sonolytic decomposition of 4-nitrophenyl acetate.^[23] This contradicts the general experience that in sonolysis, free-radical-induced and, in the case of volatile substrates, pyrolytic decomposition pathways are commonplace.^[10, 14, 24, 25] In order to settle this question, a detailed product study of the sonolysis of 4-nitrophenyl acetate, which has been lacking to date, was undertaken. We show that this system is far from being a specific probe for a transient appearance of local supercriticality in sonicated water.

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Experimental Section

4-Nitrophenyl acetate (Fluka, >99%) was used without further purification. Solutions were prepared in Milli-Q-purified (Millipore) water. The rate of dissolution of 4-nitrophenyl acetate in water is low at room temperature. Owing to the compound's relatively fast hydrolysis at elevated temperatures,^[19] it is not feasible to accelerate the dissolution by heating. Complete dissolution to a 10^{-4} M solution was achieved at room temperature after overnight stirring.

For sonication, a laboratory sonicator was used (USW 15-02 and 1040L, Allied Signal Elac, Kiel, Germany) with a capacity of 0.5 dm^3 . Typically, the experiments were carried out in small vessels containing 8 mL solution which were purged with argon prior to sonication; such a vessel was immersed at a fixed position in the water-filled sonicator (a more detailed description of the experimental arrangement can be found in ref. [26]). The sonicator can be operated at a variety of frequencies; for this study we chose 321 kHz at a typical water-absorbed power of 170 W kg^{-1} as measured by calorimetry.^[26] Under these conditions, a product buildup rate of $1 \times 10^{-6} \text{ mol dm}^{-3} \text{ min}^{-1}$ corresponds to a G value of $9.8 \times 10^{-11} \text{ mol J}^{-1}$. In the following, yields are given in terms of G values (energy yields). The sonolytic OH-radical yield was determined with terephthalate and iodide dosimeters.^[27] γ -Irradiation was carried out in a ^{60}Co - γ panoramic source (Nuclear Engineering). The γ dose rate was determined by Fricke dosimetry (cf. refs. [28, 29]).

Samples were analyzed by HPLC (Merck-Hitachi L4500 diode array detector) on a reversed-phase column (Merck, Nucleosil 100 5C18) with water/methanol/acetic acid (60:40:1 mixture) as eluent. 2-Hydroxy-4-nitrophenyl acetate was characterized and quantitatively determined as 4-nitrocatechol after hydrolysis (reference material for this was available from Fluka).

Nitrite and nitrate were measured by high-performance ion chromatography (HPIC, Dionex) on an AS-9 column (Dionex) and $1.7 \times 10^{-3} \text{ mol dm}^{-3} \text{ HCO}_3^- / 1.8 \times 10^{-3} \text{ mol dm}^{-3} \text{ CO}_3^{2-}$ as eluent. When very low, nitrite concentrations were determined spectrophotometrically.^[30] HPIC failed in the determination of acetate ion, since 4-nitrophenyl acetate is partially hydrolyzed under the conditions that are suitable for the determination of acetate (AS-9 column, $5 \times 10^{-4} \text{ mol dm}^{-3} \text{ HCO}_3^-$ as eluent). However, acetate ion could be quantitatively determined by isotachopheresis (Merck L-103) with the two-column coupling technique, where solutions containing 0.05% TRITON X-100 and 10^{-2} or $5 \times 10^{-3} \text{ mol dm}^{-3}$ of HCl as well as 2×10^{-2} or $10^{-2} \text{ mol dm}^{-3}$ of histidine served as leading electrolytes. The terminating electrolyte consisted of potassium glutamate and histidine (both $10^{-2} \text{ mol dm}^{-3}$).^[31] The acetate was determined immediately after completion of the radiolysis or sonolysis experiment. To achieve sufficiently short irradiation times, a high dose rate (5 Gys^{-1}) was used.

Volatile hydrocarbons were determined gas-chromatographically by performing head-space analysis. Carbon monoxide, carbon dioxide, and hydrogen were also measured by means of gas chromatography.^[32] Formaldehyde and acetaldehyde were identified and quantified as pentafluorobenzyl oximes,^[33] and hydrogen peroxide with molybdate-activated iodide.^[34] In the product studies, conversions below 30% led to linear yield-versus-dose relationships, as shown in Figure 1.

The reaction of the OH radical with 4-nitrophenyl acetate is fast. The rate constant was determined by means of pulse radiolysis^[35] at $2.9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ by following the build-up of the OH-radical adduct at its maximum (410 nm) as a function of the 4-nitrophenyl acetate concentration.

Results and Discussion

Free-radical formation in the γ -radiolysis and sonolysis of aqueous solutions: In the sonolysis of aqueous solutions, beside cavitationaly induced thermolytic processes involving certain solutes, the OH radical plays an important role in the chemical transformation of such solutes as are reactive toward this species, that is to say, practically all organic compounds. In order to separate the role of the aqueous-phase OH-radical-

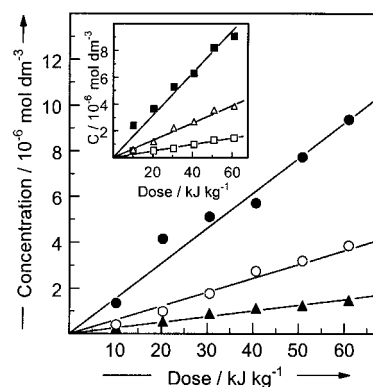
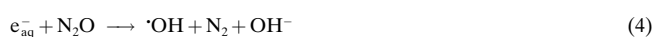
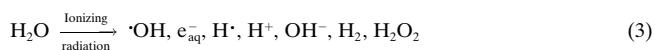


Figure 1. Sonolysis of argon-saturated solutions of 4-nitrophenyl acetate ($10^{-4} \text{ mol dm}^{-3}$). Product yields as a function of absorbed dose: 2-hydroxy-4-nitrophenyl acetate in the absence (\circ) and presence (\bullet) of the oxidant IrCl_6^{2-} , 4-nitrocatechol (\blacktriangle) (in the absence of oxidant). Inset: nitrite (\blacksquare), acetate (\triangle), and nitrate (\square); all in the absence of oxidant.

induced chemistry from the other chemical effects of ultrasound, it is useful to look at the radiation-chemical behavior of a substrate as a model situation. Ionizing radiation generates OH radicals and other free-radical and ionic species [Eq. (3)]. The radiation chemistry of dilute aqueous solutions is well understood.^[36] The conditions of the γ -irradiation were chosen such that $G(\cdot\text{OH}) = 5.8 \times 10^{-7} \text{ mol J}^{-1}$ and $G(\text{H}\cdot) = 0.6 \times 10^{-7} \text{ mol J}^{-1}$ [N_2O saturation is used to effect reaction (4)].^[36]



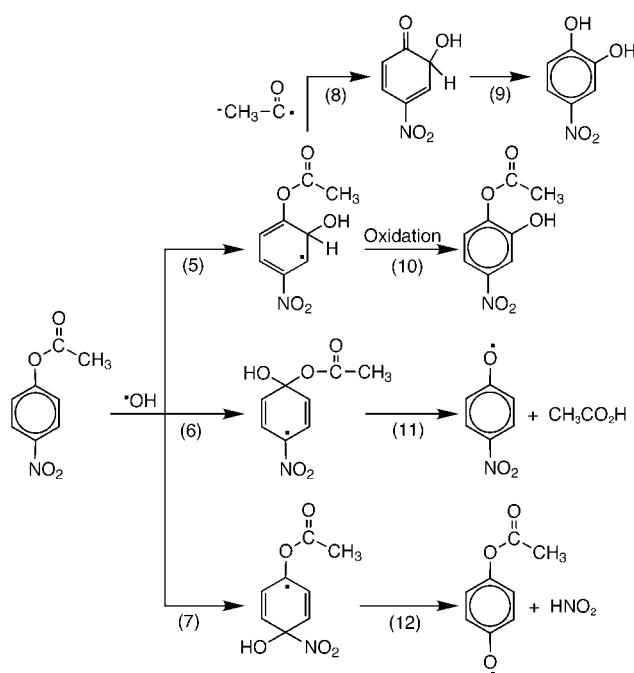
Sonication of argon-saturated aqueous solutions generates OH radicals and H atoms [Eq. (1)]. In comparison with the OH radicals, a considerably smaller number^[9, 37, 38] (about one quarter)^[26, 27] of H atoms reach the solution. This is thought to be so because of two processes: the recombination of H atoms in the gas phase and a fast conversion of hot H atoms into OH radicals in an (endothermic) reaction with water molecules.^[39] Water vapor is probably present in excess over the water radicals (a different view is given in ref. [40]), even at the late-collapse stage of the cavitational bubbles.^[41] At the surface of the collapsed bubble the OH-radical concentration is remarkably high; we recently estimated this concentration, in the absence of a volatile scavenger and at the frequency used in this study,^[27] to be about $10^{-2} \text{ mol dm}^{-3}$; this is similar to a previous estimate.^[42] At low scavenger concentrations, a considerable proportion of these OH radicals recombine to yield H_2O_2 . At higher scavenger concentrations, an increasing proportion of the OH radicals is scavenged and the H_2O_2 yield progressively reduced. This scavenging process follows non-homogeneous kinetics and is therefore difficult to assess, as the boundary conditions (for example, the exact spatial distribution of the OH radicals) are not known. The yield of scavengeable OH radicals can be obtained by the use of a suitable nonvolatile dosimeter system.^[26, 27] The total sonolytic OH-radical yield [$G(\cdot\text{OH}) + 2G(\text{H}_2\text{O}_2)$] is $16 \times 10^{-10} \text{ mol J}^{-1}$. The OH-radical yield in the presence of a nonvolatile solute such as terephthalate or iodide depends on the solute's

scavenging capacity (which is the product of the concentration of the scavenger and its OH-radical reaction rate constant). The scavenging capacity of a $10^{-4} \text{ mol dm}^{-3}$ 4-nitrophenyl acetate solution would be $3 \times 10^5 \text{ s}^{-1}$ if no allowance was made for hydrophobic enrichment^[27, 43] at the bubble interface. At this scavenging capacity, $G(\cdot\text{OH}) \approx 1.5 \times 10^{-10} \text{ mol J}^{-1}$ is scavenged in the aqueous phase and $G(\text{H}_2\text{O}_2) \approx 6.5 \times 10^{-10} \text{ mol J}^{-1}$ is observed.^[26, 27]

In the absence of a scavenger, values of $G(\text{H}_2\text{O}_2) = 6.9 \times 10^{-10} \text{ mol J}^{-1}$, $G(\text{H}_2) = 9.8 \times 10^{-10} \text{ mol J}^{-1}$, and $G(\text{O}_2) = 1.4 \times 10^{-10} \text{ mol J}^{-1}$ have been reported.^[26] Thus the sonolytic OH-radical yield is about three orders of magnitude lower than the radiolytic yield in N_2O -saturated solutions ($G(\cdot\text{OH}) = 5.8 \times 10^{-7} \text{ mol J}^{-1}$), but in sonolysis the effective OH-radical density in the reaction zones is considerably higher and the reaction zones themselves are much larger.

γ -Radiolysis of 4-nitrophenyl acetate: The primary reactions of the OH radical with 4-nitrophenyl acetate are similar to those with its parent 4-nitrophenol.^[44–48] Further details are reported elsewhere.^[49] For the present purpose, it suffices to note that there is an 84% likelihood of an OH-radical adding to the *ortho* position [reaction (5) in Scheme 1]. The extent of addition to the *para* and *ipso* positions is reflected by the nitrite and acetate yields (ca. 7 and 10%, respectively; see reactions (7)/(12) and (6)/(11) in Scheme 1). Similarly low proportions of *ipso* addition occur with anisol^[50] and phenylalanine.^[51] In the present case, the OH-radical balance leaves little room for an addition to the *meta* position, in agreement with what is found for the parent 4-nitrophenol.^[44–48, 52]

The yields of some radiolysis products of 4-nitrophenyl acetate have been extracted from ref. [49] and are shown in Table 1. The radiolytic free-radical mass balance with respect to $G(\cdot\text{OH})$, based on the products that have been identified in



Scheme 1.

Table 1 (excluding radical recombination products), is poor in the absence of the oxidant IrCl_6^{2-} . This contrasts with the case of 4-nitrophenol, where the parent itself acts to oxidize its OH-adduct radical.^[52]

Table 1. γ -Radiolysis of 4-nitrophenyl acetate ($10^{-3} \text{ mol dm}^{-3}$) in N_2O -saturated aqueous solution at a dose rate of 5 Gys^{-1} and its sonolysis in argon-saturated aqueous solutions ($10^{-4} \text{ mol dm}^{-3}$).

Product	Radiolytic yield [$10^{-7} \text{ mol J}^{-1}$]	Sonolytic yield [$10^{-11} \text{ mol J}^{-1}$]
2-hydroxy-4-nitrophenyl acetate	0.76 0.63 ^[a] (4.9) ^[b]	6.1 (15.6) ^[c]
4-nitrocatechol	0.8 0.24 ^[a]	2.5
acetate	0.68	6.5
4-nitrophenol	absent	absent
nitrite	0.4	15
nitrate	absent	2.4
methane	absent	0.1–0.2 ^[d]
acetylene	absent	0.4
ethene	absent	0.09
carbon monoxide	absent	59
carbon dioxide	absent	21
formaldehyde	absent	0.15
acetaldehyde	absent	0.04
hydrogen	n.d.	148
hydrogen peroxide	n.d.	33
consumption	n.d.	57 (53) ^[a]

n.d. = not determined. a) Dose rate $1.7 \times 10^{-2} \text{ Gys}^{-1}$. b) Oxidant $5 \times 10^{-4} \text{ mol dm}^{-3} \text{ IrCl}_6^{2-}$. c) Oxidant $1 \times 10^{-3} \text{ mol dm}^{-3} \text{ IrCl}_6^{2-}$. d) Owing to its short retention time under these analytical conditions, the methane signal was partially overlain by the GC-column switch-on pressure jump.

Sonolysis of 4-nitrophenyl acetate: Argon-saturated aqueous solutions of 4-nitrophenyl acetate ($10^{-4} \text{ mol dm}^{-3}$) were sonicated at 321 kHz. Substrate degradation (followed by HPLC) has first-order kinetics, as one would expect for a pyrolytic process where the amount of substance exposed to the reaction conditions is proportional to its bulk concentration; likewise, for example, for a situation in which reactive radicals such as $\cdot\text{OH}$ react at similar specific rates with a given substrate and its reaction products alike. Thus in complex reaction systems such as those encountered in sonolysis, first-order behavior is by no means indicative of a simple non-radical process such as hydrolysis. For comparison, the same experiment was carried out with 4-nitrophenol. The degradation kinetics are practically the same for both compounds (Figure 2).

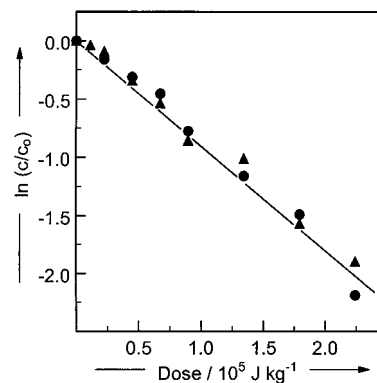


Figure 2. First-order plot for the sonolytic degradation of 4-nitrophenol (▲) and 4-nitrophenyl acetate (●) in argon-saturated aqueous solutions ($10^{-4} \text{ mol dm}^{-3}$), pH 6.5; 321 kHz, 150 W kg^{-1} .

The products generated by the addition of the OH radical to the aromatic solute, namely 2-hydroxy-4-nitrophenyl acetate, 4-nitrocatechol, acetate, and nitrite [Scheme 1, Eqs. (5)–(12)], are observed under both radiolytic and sonolytic conditions (Table 1). The nitrite yield is considerably increased relative to γ -radiolysis, a fact that indicates thermolytic cleavage of the C–N bond. Most characteristically, the dominance of carbon monoxide and carbon dioxide and the appearance of acetylene indicate that extensive ‘deep aquaplyrolysis’ (oxidation of the organic material by H₂O, which is in turn reduced to H₂) takes place under sonolysis. This is reflected by the large hydrogen yield recorded in Table 1.

In the present context, the crucial finding is the low yield of acetate and the absence of the sonolytic formation of 4-nitrophenol. At the start of sonolysis, the 4-nitrophenol concentration does not exceed 3% of the 4-nitrophenyl acetate, and it does not increase upon sonication. The initial 4-nitrophenol component is because of both an impurity in the 4-nitrophenyl acetate and some hydrolysis during dissolution of the latter. The conjecture that 4-nitrophenol, once produced, might then be *preferentially* destroyed can be ruled out. As Figure 2 shows, the specific rate of disappearance of 4-nitrophenol does not exceed that of its acetate.

Notwithstanding the convincing experimental evidence of the absence of a hydrolytic component in the sonolytic degradation of aqueous 4-nitrophenyl acetate, an attempt to estimate the relative importance of the hydrolytic versus the OH-radical-induced component (excluding the pyrolytic component) of the decomposition may still be made (see Appendix). This *also* suggests that the uncatalyzed as well as the base- (OH⁻) catalyzed hydrolysis at the fringe of the cavitation bubble is not competitive with the OH-radical-induced reaction. The conclusion is that the 4-nitrophenyl acetate system is not capable of probing the domain of transient supercriticality (this remains true for the conceivable case that the pyrolytic destruction of any nitroaromatic, be it substrate or product, within the cavitation bubble is close to 100%). In fact, any presumed state of supercriticality is simply not persistent enough to permit it to make a sizeable contribution, on account of hydrolysis, to the sonolysis products of any hydrolyzable compound, relative to the homolytic/pyrolytic decomposition pathways, given the kinetic characteristics of hydrolytic reactions.

Appendix

Assuming the hydrolysis to be noncatalyzed, on the basis of an activation energy of 78 kJ mol⁻¹ and a room-temperature rate constant of $8 \times 10^{-7} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$,^[19, 22] and assuming linear Arrhenius behaviour, one estimates rate constants $k(900 \text{ K}) = 8.6 \times 10^2 \text{ s}^{-1}$ and $k(1200 \text{ K}) = 1.1 \times 10^4 \text{ s}^{-1}$, which correspond to half-lives of $t_{1/2}(900 \text{ K}) \approx 10^{-3} \text{ s}$ and $t_{1/2}(1200 \text{ K}) \approx 6 \times 10^{-5} \text{ s}$. Since the duration of the ‘hot spot’ is less than 1 μs , one may conclude that, at 1200 K, about 1% of the 4-nitrophenyl acetate contained in the supercritical domain should be hydrolyzed. On the other hand, in the OH-radical-induced reaction, the concentration of OH radicals at the bubble interface is on the order of $10^{-2} \text{ mol dm}^{-3}$.^[27, 43] At 1200 K, $k(\text{OH} + 4\text{-nitrophenyl acetate})$ must be above $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Thus the rate constant for the disappearance of the substrate is 10^8 s^{-1} or greater. This means that the half-life of the OH-induced decomposition is

expected to be well below the microsecond range, and therefore several orders of magnitude shorter than that of the uncatalyzed hydrolysis. Can OH⁻-catalyzed hydrolysis be faster under these conditions? It is known that the ion product of supercritical water, below a pressure of about a thousand bar, sharply decreases with increasing temperature (at constant pressure), while it increases with increasing pressure (at constant temperature).^[53] Thus at 1200 K and 1000 bar,^[53] $k_w = 10^{-16.2} \text{ mol}^2 \text{ dm}^{-6}$ (where $\text{OH}^- \approx 10^{-8} \text{ mol dm}^{-3}$). At room temperature, $k(\text{OH}^- + 4\text{-nitrophenyl acetate}) \approx 12 \times \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.^[19] The activation enthalpy for OH⁻-catalyzed hydrolysis is reported to be 43 kJ mol⁻¹,^[22] thus at 1200 K one estimates $k(\text{OH}^- + 4\text{-nitrophenyl acetate}) \times [\text{OH}^-] \approx 5 \times 10^6 \times 10^{-8} \text{ s}^{-1} \approx 5 \times 10^{-2} \text{ s}^{-1}$. Therefore, $t_{1/2}$ is on the order of seconds. Moreover, the supercritical domain is diluted with the operating gas, which means that the ion-product will be much smaller still.^[54]

Acknowledgment

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- [23] In its disregard of the importance of free-radical-induced decomposition pathways, this hypothesis is reminiscent of a postulate regarding the ‘hydrolysis’ of acetaldehyde dimethyl acetal by ionizing radiation (D. R. Smith, W. H. Stevens, *Nature (London)* **1963**, *200*, 66–67), which claimed that the relatively high (compared to the bulk) concentration of H⁺ in the small domains of energy deposition by the ionizing radiation (the so-called spurs) leads to the formation of acetaldehyde upon the hydrolysis of the acetal. It is easy to see why the effect of this transient local increase of acidity must be irrelevant

- in the case of organic compounds as substrates compared with that of free radicals ($\cdot\text{OH}$ practically always, e_{aq}^- and $\text{H}\cdot$ in many cases). $G(\text{H}^+)$ at $3.5 \times 10^{-7} \text{ mol J}^{-1}$ and $G(\cdot\text{OH})$ at $2.9 \times 10^{-7} \text{ mol J}^{-1}$ are of comparable magnitude, but whereas the rate constants of OH-radical reactions in almost all cases are above $10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (G. V. Buxton, C. L. Greenstock, W. P. Helman, A. B. Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513–886), the rate constants of proton-catalyzed hydrolysis are practically always below $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (M. M. Kreevoy, R. W. Taft, *J. Am. Chem. Soc.* **1955**, *77*, 5590–5595). Thus, the hydrolytic effect of ionizing radiation is smaller than the free-radical effect by several orders of magnitude. (Nevertheless, this erroneous conception is found in some radiation-chemistry textbooks, for example ref. [28]). Thus, as expected, acetaldehyde formation in the acetal system is a free-radical-induced reaction (R. A. Basson, P. M. Champion, *Nature* **1966**, *211*, 1398–1399; M. N. Schuchmann, H.-P. Schuchmann, C. von Sonntag, *J. Am. Chem. Soc.* **1990**, *112*, 403–407).
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