Sonolysis of *tert*-butyl alcohol in aqueous solution

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A product study of the sonolysis of the volatile substrate *t*-butanol in aqueous solution indicates that substrate decomposition is practically completely determined, even at concentrations as low as millimolar, by oxidative pyrolysis going on in the gas phase within the collapsing cavitational bubble. OH-Radical-induced reactions in solution are insignificant since the volatility of this substrate, its gas-phase concentration within the bubble enhanced by a certain degree of hydrophobicity, causes OH radicals generated thermolytically from water vapour to be intercepted before they can reach the aqueous phase. The nature of the products, as well as the *t*-butanol-concentration dependence of the product yields, can be qualitatively explained on the basis of the *t*-butanol-pyrolysis mechanism. Kinetic considerations involving the relative yields of the pyrolysis products ethane, ethylene and acetylene lead to an estimate of a value of 3600 K for the average pyrolysis temperature at a *t*-butanol bulk concentration of 10^{-3} molar.

The action of sound of sufficiently high frequency on a liquid may lead to the creation of small voids in the interior of the liquid ("cavitation") whose size oscillates with the frequency of the sonic field until their eventual collapse (*cf.* refs. 1–4). As these cavitational bubbles are formed, they fill with the vapours of the liquid (solvent and volatile solutes including dissolved gases; saturation with a gas facilitates cavitation). As the bubbles contract or collapse, their contents are heated more or less adiabatically, and depending on the thermodynamic properties of the vapour mixture (*e.g.* c_p/c_v; *cf.* ref. 4), sufficiently high temperatures, several thousand degrees, may be reached,[5–12] so that partial thermolysis of the constituents of the vapour may occur within the bubble (*cf.* refs. 1–4). A comprehensive mathematical analysis of cavitational-bubble evolution which includes the effect of chemical transformations within the bubble has appeared very recently.[12]

Aqueous solutions can be considered as a special case. The thermolysis of the water molecule leads to the formation of the OH radical and the H atom [reaction (1)].[13–16] Moreover, oxygen

$$\mathrm{H_2O} \xrightarrow{\Delta} \mathrm{H}^\bullet + {}^\bullet\mathrm{OH} \qquad (1)$$

may also be formed in a sequence of subsequent reactions [*e.g.* reactions (2)–(4)].[17,18] This means that in aqueous solutions the sonolytic process can never be strictly anoxic.

$${}^\bullet\mathrm{OH} + \mathrm{H}^\bullet \longrightarrow \mathrm{H_2} + \mathrm{O} \qquad (2)$$

$$2\,{}^\bullet\mathrm{OH} \longrightarrow \mathrm{H_2O} + \mathrm{O} \qquad (3)$$

$$\mathrm{O} + {}^\bullet\mathrm{OH} \longrightarrow \mathrm{O_2} + \mathrm{H}^\bullet \qquad (4)$$

The OH radical in particular is a most reactive species, and in so far as OH radicals penetrate into the liquid phase they may react in this medium with a solute, apart from undergoing recombination in the boundary layer of the collapsing cavitational bubble where their concentration may reach values of 10^{-2} mol dm^{-3}.[18,19] Thus even in dilute solutions only a small fraction of the OH radicals escape from the liquid boundary zone and reach the bulk of the liquid.[19] OH-Radical chemistry in aqueous solution has been studied extensively by radiolysis (*cf.* refs. 20, 21). A further complexity arises when hydrophobicity effects come into play as is the case with many non-ionic organic solutes. This leads to the enrichment of a solute in the boundary layer and a corresponding enhancement of the relative importance of boundary-layer OH-radical scavenging *versus* the reactions in the bulk.[18,19] In the case of volatile solutes, a large proportion of the OH radicals will be captured already "at the source", so that only a correspondingly smaller number make it to the boundary layer.[19]

The volatile solute *tert*-butyl alcohol (*t*-butanol) can be employed to gauge the extent of the OH-radical shortfall due to intra-bubble gas-phase radical scavenging as well as to the lowering of the intra-bubble temperature since its value c_p/c_v is not far from unity. The *t*-butanol-concentration dependence of this shortfall has been shown before.[19] In the present work, we wish to present further results, especially regarding the *products* of aqueous *t*-butanol sonolysis.

At the elevated temperatures prevailing within the core region of the collapsing cavitational bubble, the partial pressure of water may be expected to be considerable. Free-radical attack at *t*-butanol may thus be initiated largely by ${}^\bullet$OH and H${}^\bullet$ effecting H-atom-abstraction [reaction (5)]. At room temperature, these *t*-butanol-derived radicals would recombine giving rise to 2,5-dimethylhexane-2,5-diol [reaction (6)] which is the

$${}^\bullet\mathrm{OH}\ (\mathrm{H}^\bullet) + \mathrm{(CH_3)_3COH} \longrightarrow \mathrm{H_2O}\ (\mathrm{H_2}) + {}^\bullet\mathrm{CH_2C(CH_3)_2OH} \qquad (5)$$

$$2\,{}^\bullet\mathrm{CH_2C(CH_3)_2OH} \longrightarrow [\mathrm{CH_2C(CH_3)_2OH}]_2 \qquad (6)$$

main product in the radiolysis of anoxic aqueous solutions of *t*-butanol.[22,23]

Gas-phase pyrolytic reactions involving the organic substrate may play an even larger part. Up to 1300 K *t*-butanol decomposes into isobutene and water in an essentially clean unimolecular process [reaction (7)]; at higher temperatures free-radical processes eventually gain the upper hand [*e.g.* reaction

$$\mathrm{(CH_3)_3COH} \longrightarrow \mathrm{H_2O} + \mathrm{CH_2{=}C(CH_3)_2} \qquad (7)$$

(8)].[24–26] The *t*-butanol-derived radical [formed *e.g.* in reaction

$$(CH_3)_3COH \longrightarrow {}^{\bullet}C(CH_3)_2OH + {}^{\bullet}CH_3 \qquad (8)$$

(5)], stable at room temperature, requires a much lower activation energy for its decomposition [*e.g.* reaction (9)] than the

$${}^{\bullet}CH_2(CH_3)_2COH \longrightarrow {}^{\bullet}CH_3 + CH_2{=}C(CH_3)OH \qquad (9)$$

parent compound, *i.e.* this sequence may be said to constitute a free-radical-induced pyrolysis process.

If high-temperature reactions were of little importance in the sonolysis of aqueous *t*-butanol, 2,5-dimethylhexane-2,5-diol should be the major product. This is, however not the case,[27] and we have therefore undertaken a more detailed study in order to elucidate some of the underlying complexities of this system.

Experimental

t-Butanol (Merck) was used without further purification. The solutions were prepared in Milli-Q-purified (Millipore) water. For sonication, a laboratory sonicator (USW 15-02 and 1040L, AlliedSignal Elac Nautik, Kiel, Germany), capacity 0.5 dm^{-3}, was used. Typically, the experiments were carried out in smaller vessels containing 8 ml solution which prior to sonication were purged with argon; such a vessel was inserted into the water-filled sonicator in the axial position through a hole in the lid, and rotated during sonication by means of a little motor and a rubber band.[28] The sonic frequency was 321 kHz at a typical absorbed power of 170 W kg^{-1}, determined by calorimetry.[28]

The yield of free OH radicals that manifest themselves in the aqueous phase was determined using 2×10^{-3} mol dm^{-3} terephthalate in the presence of 2×10^{-4} mol dm^{-3} $IrCl_6^{2-}$.[19,28,29] Hydrogen peroxide was determined spectrophotometrically by molybdate-activated iodide[30] in separate experiments.

Formaldehyde was determined by the Hantzsch method.[31] Acetaldehyde and acetone were derivatized with 2,4-dinitrophenylhydrazine and determined spectrophotometrically after separation by HPLC (125 mm Nucleosil-C18 Merck-Darmstadt, eluent: acetonitrile–H_2O (3:2); Merck-Hitachi L 4500, diode-array detector).[32] Acetate was determined by ion chromatography (Dionex DX-100; AS9-SG column, eluent: 5×10^{-4} mol dm^{-3} $NaHCO_3$).

Volatile hydrocarbons were determined gas-chromatographically, taking aliquots from the head-space (10 ml). Under these experimental conditions, those products separate from the liquid practically completely, apart from acetylene whose yield may therefore be slightly underestimated. Carbon monoxide, carbon dioxide and hydrogen were also measured by gas chromatography.[33] The consumption of *t*-butanol has been determined by gas chromatography directly from the sonicated solution. There are indications that other hydroxy compounds beside 2,5-dimethylhexane-2,5-diol (determined by gas chromatography as its trimethylsilyl ether) are also produced, among them apparently propanediols and glycerol. Their identification and determination were not pursued. There are experimental difficulties in determining diols quantitatively. The trimethylsilylation approach involves evaporation to dryness or freeze-drying of the samples which leads to losses of these compounds on account of their volatility. Therefore, an isomer, octane-1,8-diol, which has a similar volatility to 2,5-dimethylhexane-2,5-diol was added as an internal standard prior to rotary evaporation.

Product yields were linear with the absorbed dose (*cf.* Fig. 1); substrate conversions did not exceed 20% at the lowest concentrations used and were usually much smaller. In the following, the yields are given in terms of "energy yields" (*G*, unit mol J^{-1}). Under the experimental conditions chosen, a product build-up rate of 2×10^{-6} mol dm^{-3} min^{-1} corresponds to a *G* value of 1.9×10^{-10} mol J^{-1}.

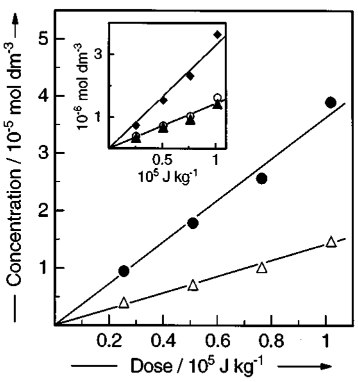


Fig. 1 Sonolysis of argon-saturated aqueous *t*-butanol solutions (10^{-3} mol dm^{-3}). Concentration (amount of product formed divided by volume of the sonicated solution) of the hydrocarbons as a function of dose: methane (●) and acetylene (△). Inset: ethylene (◆), ethane (○) and isobutene (▲).

Results and discussion

OH-Radical formation in the sonolysis of aqueous solutions

Sonication of aqueous solutions creates OH radicals and H atoms [reaction (1)]. In the absence of reactive volatile solutes, one finds that compared to OH radicals, a considerably smaller number[14,34,35] (about one quarter)[19,28] of H atoms reach the liquid. This is thought to be due to two processes, *i.e.* recombination of H atoms in the gas phase [reaction (10)] and a conver-

$$2\,H^{\bullet} \longrightarrow H_2 \qquad (10)$$

sion of H atoms into OH radicals in the pyrolytic environment [reaction (11)].[36]

$$H^{\bullet} + H_2O \longrightarrow H_2 + {}^{\bullet}OH \qquad (11)$$

At the gas–liquid interface of the collapsing cavitational bubble, the OH-radical concentration is remarkably high;[18] at the sonic frequency used in this study we have estimated their concentration at about 10^{-2} mol dm^{-3} across this layer.[19] Here, a considerable number of these OH radicals will recombine, yielding H_2O_2 [reaction (12)]. In the presence of an OH radical

$$2\,{}^{\bullet}OH \longrightarrow H_2O_2 \qquad (12)$$

scavenger in this layer, part of the OH radicals will be scavenged; hence the H_2O_2 yield will be reduced. This scavenging process follows difficult-to-assess non-homogeneous kinetics, as the boundary conditions (*e.g.* spatial distribution of the OH radicals) are not known. The yield of scavengeable OH-radicals in the liquid can be obtained by using a suitable non-volatile dosimeter compound, *e.g.* terephthalate.[19,28] The use of the non-reactive monoatomic gas argon and the exclusion of air ensure the suppression of large-scale oxidative side reactions.

In the present study, the yield of OH radicals that manifest themselves in the liquid has been determined with the terephthalate and iodide dosimeters. The total yield [$G({}^{\bullet}OH) + 2\,G(H_2O_2)$] equals 16×10^{-10} mol J^{-1}.[19,28] In the presence of a non-volatile solute such as terephthalate or iodide, $G({}^{\bullet}OH)$ (*i.e.* of ${}^{\bullet}OH$ that escape recombination) depends on the scavenging capacity (*i.e.* the product of the concentration of the scavenger and its OH-radical rate constant).[28] The higher the scavenging capacity, the lower $G(H_2O_2)$. In the absence of any scavenger, $G({}^{\bullet}OH)$ is zero, and $G(H_2O_2) = 6.9 \times 10^{-10}$ mol J^{-1} (smaller than the expected value of 8×10^{-10} mol J^{-1}, see above, because of the destruction of some H_2O_2 by ${}^{\bullet}OH$),[19,28] $G(H_2) =$

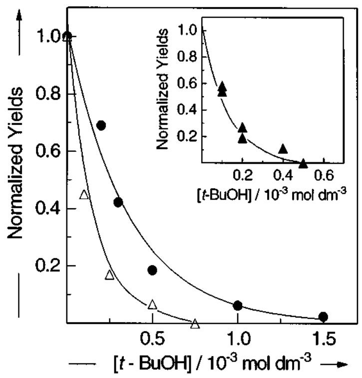


Fig. 2 Sonolysis of argon-saturated aqueous *t*-butanol in the presence of 2×10^{-3} mol dm^{-3} terephthalate. Normalized yields of OH radicals as determined by the terephthalate dosimeter (●) and H_2O_2 (△) as a function of the *t*-butanol concentration. Inset: suppression of the H_2O_2 yield in the absence of terephthalate (▲).

9.8×10^{-10} mol J^{-1}, and $G(O_2) = 1.4 \times 10^{-10}$ mol J^{-1} have been obtained.

The influence of *t*-butanol

The use of *t*-butanol as an OH-radical-scavenging solute leads to a drastic change in the dependence of $G(H_2O_2)$ on the scavenger concentration. The H_2O_2 yield is already halved at a *t*-butanol bulk concentration of 1×10^{-4} mol dm^{-3} (*cf.* inset in Fig. 2, for a similar value see ref. 37). This concentration corresponds to the low scavenging capacity of 6×10^4 s^{-1} ($k_2 = 6 \times 10^8$ dm^3 mol^{-1} s^{-1}).[21] For an ionic scavenger alone to produce the same effect, a scavenging capacity a thousandfold greater would be required.[19]

The explanation of this apparent discrepancy is as follows. One of the reasons is a hydrophilic enrichment in the boundary layer of the cavitational bubble. However, while *t*-butanol is moderately hydrophobic so that some enrichment takes place at the bubble surface, this effect is far from sufficient to account for the strong suppression of H_2O_2 formation as the enrichment is only seventeen-fold compared to the bulk concentration; the line of argument providing an estimated value for the enrichment factor is presented in the Appendix (*cf.* ref. 19).

A *t*-butanol concentration of 1.7×10^{-2} mol dm^{-3} (in the boundary layer, which corresponds to a bulk concentration of 1×10^{-3} mol dm^{-3}) represents a scavenging capacity of 1.1×10^7 s^{-1}. Now in order to cut the H_2O_2 yield in half, a scavenging capacity of 7.7×10^7 s^{-1}, using a non-volatile ionic compound such as iodide or terephthalate, is required (*cf.* ref. 19 and Fig. 2 therein). To achieve the same effect under purely solution-kinetics conditions with *t*-butanol, a concentration of 0.13 mol dm^{-3} would be necessary. As a boundary-layer concentration, this corresponds to a bulk concentration of 7.6×10^{-3} mol dm^{-3} which is far beyond the *t*-butanol bulk concentration actually needed (near 1×10^{-4} mol dm^{-3}, see Fig. 2) to reduce the H_2O_2 yield by half. This means that in the case of *t*-butanol, hydrophobic enrichment of the boundary layer cannot serve as the sole explanation for the enhancement of the OH-radical scavenging effect, compared to what is known from radiation chemistry.

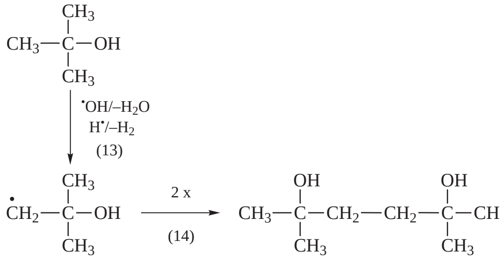
Fig. 2 shows the yields of the OH radicals scavenged, as determined by the terephthalate dosimeter,[28,29] and of the remaining H_2O_2. It can be seen that practically no OH radicals reach the liquid phase beyond a *t*-butanol concentration of 1.5×10^{-3} mol dm^{-3}; at that point, the ratio of the scavenging capacities of terephthalate and *t*-butanol is about 3, *i.e.* most of the OH radicals that still reach the liquid phase actually react with the terephthalate and are thus registered. The data in Fig. 2 can be used to estimate[19] the proportion of OH radicals that are available to react with *t*-butanol in the absence of any other scavenger. At a bulk concentration of 10^{-3} mol dm^{-3} this is only 1 per cent of the number that reach the liquid in the *absence* of *t*-butanol. It turns out that this value is in fair agreement with the experimental yield of 2,5-dimethylhexane-2,5-diol formed under these conditions (see Table 1).

Table 1 Sonolysis of argon-saturated *t*-butanol solutions (1×10^{-3} mol dm^{-3}): some products and their *G* values

Product	*G* value/10^{-10} mol J^{-1}
2,5-Dimethylhexane-2,5-diol	0.03
Methane	3.8
Ethane	0.2
Ethylene	0.4
Acetylene	1.5
Propane	0.02
Propene	0.1
Isobutene	0.14
Formaldehyde	1.6
Acetaldehyde	0.7
Acetone	3.4
Acetate	0.3
Carbon monoxide	36
Carbon dioxide	8.5
Hydrogen	79
t-Butanol consumption	19

Product studies

Before turning to the multitude of products that are formed upon sonication of argon-saturated aqueous solutions of *t*-butanol, the value estimated[19] for the yield of OH radicals that cross from the interior of the cavitational bubble into the liquid boundary layer is to be compared against the experiment. The OH-radical-induced decomposition of *t*-butanol in aqueous solution[22] is known to lead almost quantitatively to the 2-hydroxy-2-methylpropyl radical which undergoes recombination, giving rise to 2,5-dimethylhexane-2,5-diol [reactions (13) and (14)].



At a *t*-butanol bulk concentration of 10^{-3} mol dm^{-3}, the formation of H_2O_2 is already completely suppressed (*cf.* inset in Fig. 2). Under these conditions the proportion of OH radicals reaching the liquid phase is not more than about 1 per cent of that observed in the absence of this solute (see above). In the absence of a volatile scavenger, $G(^{\bullet}OH)_{total} \approx 16 \times 10^{-10}$ mol J^{-1}: the maximum possible number of OH radicals reach the aqueous phase.[19,28] In argon-saturated solution with *t*-butanol being the only scavenging solute, one therefore expects a *G* value of merely 0.16×10^{-10} mol J^{-1} for the OH-radical-induced decomposition of *t*-butanol in the aqueous phase. Given that under these conditions the dominant product is 2,5-dimethylhexane-2,5-diol, formed with the stoichiometry implied by reactions (13) and (14), a *G* value of about 0.08×10^{-10} mol J^{-1} would be expected for this diol. In fact, the *G* value of this product observed under these conditions is about 0.03×10^{-10} mol J^{-1} (Table 1), *i.e.* lower but not widely different.

Fig. 3 and Table 1 give an impression of the variety and quantity of the products formed upon sonication of a dilute aqueous *t*-butanol solution. Methane and the C_2 hydrocarbons taken together predominate among the hydrocarbon products.

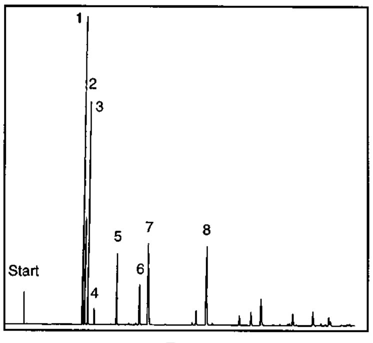


Fig. 3 Gas chromatogram of volatile products from the sonolysis of an argon-saturated aqueous *t*-butanol solution (5×10^{-2} mol dm^{-3}, dose: 6.12×10^4 J kg^{-1}): methane (1), ethane (2), ethylene (3), propane (4), propene (5), cyclopropane (6; tentative. Cyclopropane is preferred over propyne as the latter is expected to elute after acetylene), acetylene (7), isobutene (8). The other peaks remain unassigned.

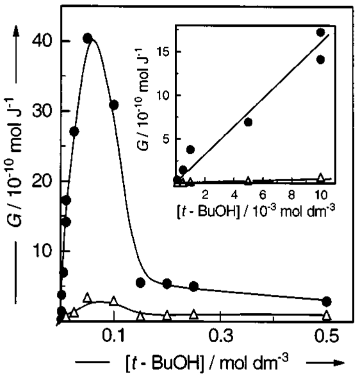


Fig. 4 Sonolysis of argon-saturated aqueous solutions of *t*-butanol: yield of methane (●) and isobutene (△) depending on the concentration of *t*-butanol. Inset: yield of these products at low concentrations of *t*-butanol.

The production of higher hydrocarbons is insignificant under the conditions that apply to Table 1 (1×10^{-3} mol dm^{-3}). Collectively at a *t*-butanol concentration of 1×10^{-3} mol dm^{-3}, their yield is estimated at about one tenth of that of acetylene, carbon atom for carbon atom. (However at higher *t*-butanol concentrations, they become relatively more important, *cf.* Fig. 3.) With the exception of 2,5-dimethylhexane-2,5-diol, the compounds listed in Table 1 are indicative of thermal cracking processes. In contrast, 2,5-dimethylhexane-2,5-diol is the key product for monitoring the extent of reaction (5) in the aqueous phase. With respect to a carbon balance, the products shown in Table 1 represent about 90 per cent of the *t*-butanol consumed.

The results shown in Table 1 force the conclusion that at this concentration almost all of the decomposition of the *t*-butanol takes place within the cavitational bubble. The products are formed for the most part in thermolytic reactions (*cf.* ref. 25). The yield of the products depends on the *t*-butanol concentration. Three domains, exemplified by the behaviour of some hydrocarbons (Figs. 4 and 5) can be distinguished, the first below about 0.05 mol dm^{-3}, the second between about 0.05 and 0.15 mol dm^{-3}, and the third above 0.15 mol dm^{-3}.

At low concentrations, the sonolytic yields increase roughly linearly with the *t*-butanol concentration. At higher *t*-butanol concentrations, the yields pass through a maximum and reach low values again at concentrations above 0.15 mol dm^{-3}. This is explained as follows. At first, the amount of pyrolysis products increases with the partial pressure of the substrate. When the partial pressure reaches a level high enough so as to begin to affect the thermal characteristics of the bubble contents through an appreciable lowering of c_p/c_v (*cf.* ref. 4), or when the substrate concentration becomes high enough to perhaps affect the intensity of cavitation (*e.g.* by reducing the surface tension, *cf.* ref. 4), the temperature reached inside the bubble will be lower, leading to a drop of product formation, as well as a change in product composition. Note that isobutene becomes *relatively* more prominent at the higher *t*-butanol concentrations (Fig. 4). This is in keeping with the observation that lower pyrolysis temperatures favour the non-radical pathway [reaction (15), *cf.* Scheme 1], while homolytic processes begin to contribute at higher temperatures [reaction (16), *cf.* Scheme 1].[24–26]

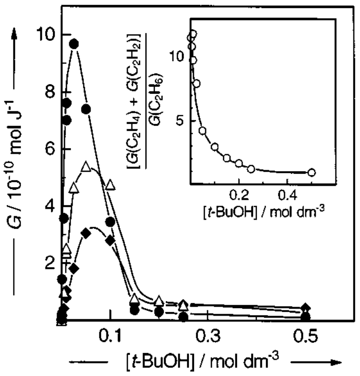


Fig. 5 Sonolysis of argon-saturated aqueous solutions of *t*-butanol. Yields of ethane (◆), ethylene (△) and acetylene (●) as a function of the *t*-butanol concentration. Inset: ratio $[G(C_2H_4) + G(C_2H_2)]/G(C_2H_6)$ as a function of the *t*-butanol concentration.

Scheme 1 indicates the main source reactions for the products methane [reactions (17), (18) and (25)], isobutene [reaction (15)], and acetone [reactions (19) and (21)]. The relatively low acetone yield suggests that this product undergoes further decomposition, *e.g.* reactions (22), (25) and (26). Acetaldehyde and acetate [*via* ketene, reaction (27)] appear in Scheme 1 as secondary products. Such products are detected eventually only in so far as they escape the core region, or because they are formed in the cooler fringe of the cavitational bubble in the first place.

Here it is important to recall that free radicals usually undergo fragmentation much more readily than their parent molecules. In the present case also, this kind of fragmentation, *e.g.* reactions (18)–(21), (24), (27) is expected to occur, eventually contributing to the formation of H_2, CH_4 and CO. However, the yield of CO is in large excess of what is expected from the pyrolysis of the *t*-butanol in the absence of an additional oxygen source. This excess is explained through the oxidation of methyl radicals by OH radicals, starting with reaction (30) (Scheme 2). Indeed, a fair hydrogen balance is achieved on the basis of the product data in Table 1 when a conversion of $^{\bullet}CH_3$ into CO is admitted into the overall reaction mechanism. (In a previous publication[19] discussing certain aspects of aqueous *t*-butanol sonolysis, this process was not taken into consideration.)

While there exists a straightforward free-radical pathway to the product CO_2 [reaction (28)], an alternative explanation

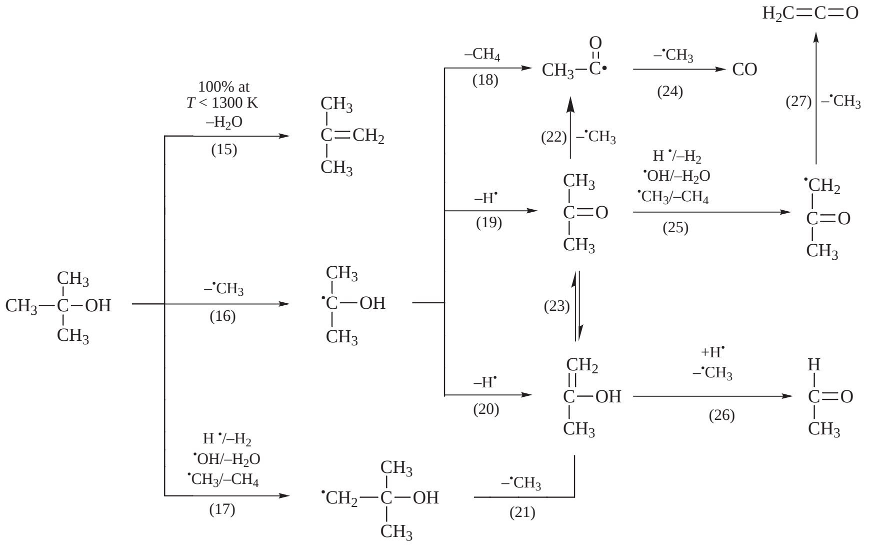
$$CO + {}^{\bullet}OH \longrightarrow CO_2 + H^{\bullet} \qquad (28)$$

could be the water–gas shift [reaction (29)]. Quantum-chemical

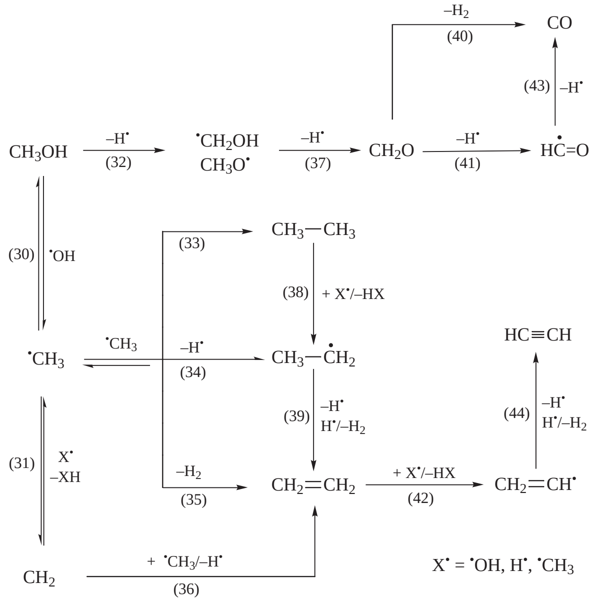
$$CO + (n + 1)\, H_2O \longrightarrow CO_2 + H_2 + n\, H_2O \qquad (29)$$

calculations have shown that the rate of this shift increases as the number of water molecules clustering around the CO molecule increases (*cf.* ref. 38). It is possible that this effect plays a role under the high-pressure conditions of the collapsing cavitational bubble.

The methyl radical occupies a central position in the formation not only of methane, but also of ethane, ethylene, and acetylene in this high-temperature, free-radical-rich



Scheme 1



Scheme 2

environment. These products (Table 1, Fig. 5) may be linked mechanistically as shown in Scheme 2 which indicates that ethane, formed in reaction (33), is not necessarily a precursor to ethylene as might be assumed from what is known about the low-temperature pyrolysis of ethane, *cf.* ref. 39 [reactions (38) and (39)]; the inverted order of importance of the ethane and ethylene yields (Table 1) argues against this. At higher-pyrolytic temperatures, ethylene can be formed directly in the reaction of two methyl radicals [reaction (35)],[36,40] or *via* carbene CH_2 [reactions (31) and (36)][41] (it appears that the direct channel to ethylene[36] becomes relatively more important compared to the carbene pathway,[41] the higher the temperature). An appreciable presence of CH_2 is expected, especially on account of reaction (31).[42,43]

Fig. 5 shows the dependence of the yields of ethane, ethylene, and acetylene on the *t*-butanol concentration. The fact that the acetylene yield appears to peak before those of ethylene and ethane is, from a thermodynamic point of view, in accordance with the expectation that higher temperatures are reached within the cavitational bubble when the *t*-butanol concentrations are small.

Interestingly, very similar results were obtained regarding the concentration dependence of the yields of the products ethane, ethylene, and acetylene in the sonolysis of argon–methane mixtures in aqueous solution (ref. 40; *cf.* Figure 5 therein). This lends strong support to the above assumption that in the sonolysis of *t*-butanol also, these three products are indeed derived from the methyl radical but not from any radical specific to the pyrolysis of a molecule containing several carbon atoms, such as *t*-butanol. In fact, the *t*-butanol-high-temperature-pyrolysis system is essentially a methyl-radical system; the stoichiometry of its thermal (free-radical) decomposition can be represented by expression (45).

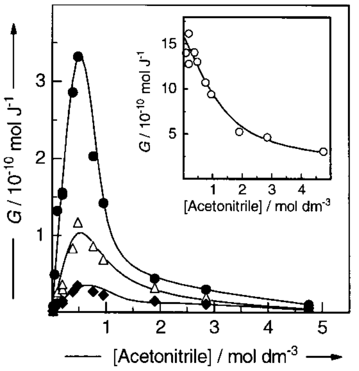


Fig. 6 Sonolysis of argon-saturated aqueous solutions of acetonitrile. Yields of ethane (◆), ethylene (△) and acetylene (●) as a function of the acetonitrile concentration. Inset: ratio [$G(C_2H_4)$ + $G(C_2H_2)$]/$G(C_2H_6)$ as a function of the acetonitrile concentration.

$$t\text{-BuOH} \longrightarrow 3\ {}^{\bullet}CH_3 + CO + H^{\bullet} \qquad (45)$$

It may be suspected generally that other substrates that involve the large-scale pyrolytic production of methyl radicals also present a similar picture. We have carried out some experiments with aqueous solutions of acetonitrile; the results are shown in Fig. 6 and corroborate this hypothesis.

Following an approach taken already by Hart, Fischer and Henglein,[40] a rough estimate may be obtained regarding the pyrolysis temperature within the cavitational bubble. Within the approximation that ethane, ethylene, and acetylene are formed in reactions (33), (35), (42), (44) (*cf.* Scheme 2) exclusively, and that these compounds are not subject to partial consumption by further reactions, the ratio [$G(C_2H_4)$ + $G(C_2H_2)$]/$G(C_2H_6)$ equals the ratio k_{33}/k_{35} of the rate constants[40] of the two parallel reactions (33) and (35) [$k_{33} = 2.4 \times 10^{14}\ T^{-0.4}$ dm^3 mol^{-1} s^{-1}, $k_{35} = 1.0 \times 10^{16} \exp(-134\ \text{kJ}/RT)$ dm^3 mol^{-1} s^{-1}].[36] Since k_{33} is only slightly, but k_{35} strongly temperature-dependent (inset in Fig. 7), this ratio must increase with increasing temperature.

Table 2 Temperatures (estimated) within the cavitational bubble as a function of the *t*-butanol concentration

[*t*-Butanol]/mol dm^{-3}	*T*/K
10^{-3}	3600
10^{-2}	3600
5×10^{-2}	3000
0.1	2800
0.25	2500
0.5	2300

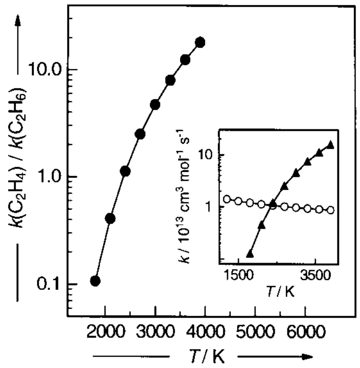


Fig. 7 Ratio of the rate constants k_{33}/k_{35} (●) as a function of the temperature. Inset: temperature-dependence of the rate constants[36] for the formation of ethane [○, reaction (33)] and ethylene [▲, reaction (35)].

In the maximum, the ratio is near 12 (Fig. 7) which corresponds to a temperature of about 3600 K. Using the data represented in Fig. 5 (inset), one arrives at an estimate for the temperatures within the cavitational bubble at various *t*-butanol concentrations (Table 2) which straddle the range from about 3600 to 2300 K. Obviously, these values represent a sort of *average* as the temperatures must be higher near the core of the collapsing cavitational bubble than near its fringe. The relatively low isobutene yield compared to the *t*-butanol consumption (Table 1; [*t*-BuOH] = 10^{-3} mol dm^{-3}) is compatible with temperatures within this range, as the pathway to isobutene [reaction (15), Scheme 1] begins to fade away above 1300 K.[24–26] Very similar conclusions as to the temperature of the "hot spot" have been drawn when methane was used as the solute[40] where the intra-cavity temperatures are estimated to vary between about 2800 and 2000 K.

The data shown in Table 2 imply that up to a bulk *t*-butanol concentration of about 10^{-2} mol dm^{-3} the thermodynamic properties of the interior of the cavitational bubble are essentially determined by the operating gas, as the average intracavity temperature appears practically independent of the substrate concentration (however, the product yield rises with the concentration within this range, see Figs. 4 and 5, as at low concentrations the partial pressure of the solute is proportional to its bulk concentration, and the amount of product is near-proportional to the solute partial pressure).

An interesting feature is shown in Fig. 8 where the concentration dependence of the H_2 and CH_4 yields is compared. The H_2 yield rises steeply at very small scavenger concentrations from the value of 9.8×10^{-10} mol J^{-1} observed in the absence of *t*-butanol, in fair chemical-balance agreement with $G(H_2O_2) = 6.9 \times 10^{-10}$ mol J^{-1} plus $G(O_2) = 1.4 \times 10^{-10}$ mol J^{-1} (see above), to peak well before methane does. Qualitatively, the explanation considers the processes in the gas phase as follows. Hydrogen-atom abstraction by $H^•$ from the substrate to form H_2 [reaction (17), Scheme 1] competes on much more favourable terms with the recombination of two H atoms (see above) than does the analogous reaction (11) with H_2O (see above). As the substrate concentration rises further, the production of organic free radicals by pyrolysis becomes more important [*e.g.* reaction (16), Scheme 1]. This provides an even more favourable channel for H-atom disappearance by recombination with such radicals, *e.g.* reaction (46), or by free-radical-displacement, *e.g.* reaction

$$H^• + {}^•CH_3 \longrightarrow CH_4 \qquad (46)$$

(26). Accordingly, the H_2 yield should drop while that of other products, *e.g.* methane, still rises.

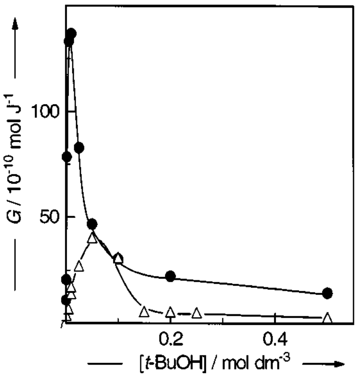


Fig. 8 Sonolysis of argon-saturated aqueous solution of *t*-butanol; yield of H_2 (●) and methane (△) as a function of the *t*-butanol concentration.

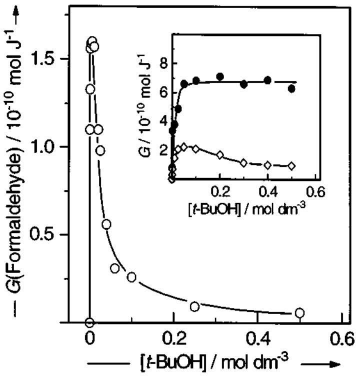


Fig. 9 Sonolysis of argon-saturated solutions of *t*-butanol. Yield of formaldehyde (○) as a function of the *t*-butanol concentration. Inset: yield of acetone (●) and acetaldehyde (◇).

The behaviour of some further products as a function of the *t*-butanol concentration is revealing. Looking at the carbonyl compounds formaldehyde, acetaldehyde and acetone, it can be seen that the formaldehyde yield (Fig. 9) peaks earlier than does the CH_4 yield (Fig. 8). This is in agreement with the hypothesis that the production of CH_2O largely depends on the recombination of ${}^•CH_3$ and ${}^•OH$ [reaction (30)]. This reaction loses its competitive edge early on to the H-atom abstraction reaction (17) as the *t*-butanol concentration increases.

The acetone and acetaldehyde yields (inset in Fig. 6) reach their highest values practically in tandem. This suggests that the formation of acetaldehyde is linked to the appearance of acetone, *e.g.* through reaction (26). At higher *t*-butanol concentrations, the acetaldehyde yield drops somewhat while that of acetone remains the same. This may be due to the diminishing presence of H atoms which would disfavour reaction (26).

A general flattening-out of the yields (*cf.* Figs. 4, 8 and 9) beyond a *t*-butanol concentration of about 0.2 mol dm^{-3} indicates that from this concentration onward, the properties of the boundary layer, including the solute fugacity, begin to resemble that of neat *t*-butanol (10 mol dm^{-3}): note that 0.2 mol dm^{-3} times the hydrophobicity factor of 17 (ref. 19) is getting close to 10 mol dm^{-3}!

A complete mechanistic elucidation of the sonolysis of aqueous solutions of *t*-butanol remains beyond reach. The temperature distribution within the cavitational bubble is expected to be inhomogeneous. A central zone where "deep" pyrolysis occurs (key product acetylene), with near-complete destruction of the organic substrate, is surrounded by progressively more temperate zones where the relatively thermolabile products such as the carbonyl compounds are to some extent preserved. Moreover, the products that are observed are largely a mix generated by a mesh of thermal and OH-radical-induced cracking processes. Nevertheless, a generally congruent picture emerges which brings together some of what is known of the mechanical action of sound on a liquid, of the chemistry of the OH radical, and of pyrolytic decomposition of water and of organic compounds.

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Appendix

We try to relate the bulk concentration of the substrate to that in the boundary layer of the cavitational bubble as follows. The concentration of a solute in the gas phase c_g above its dilute aqueous solution of concentration c_w is given by expression (47)

$$c_g = \frac{c_w}{\gamma} \qquad (47)$$

(ref. 44; this reference contains fugacity data, characterized by γ, for various solutes), and corresponds to a partial pressure p according to expression (48).

$$p = c_g RT \qquad (48)$$

Ideally in the hypothetical state of the absence of hydrophobic or hydrophilic interaction, the vapour pressure of a solute is proportional to its molar fraction x in the surface layer of the solution [expression (49)]. On the other hand, in

$$\frac{p}{p_{\text{neat}}} = x \qquad (49)$$

dilute solution x is given in terms of concentrations by expression (50) where c represents the solute concentration in the gas/liquid boundary layer and c_{H_2O} equals 55.5 mol dm^{-3}.

$$x = \frac{c}{c_{H_2O}} \qquad (50)$$

The vapour pressure of the neat solute p_{neat} at the temperature t (in centigrade) can be represented by the Antoine equation [expression (51)] where A, B and C are constants that are specific for a solute.[45]

$$\log p_{\text{neat}} = A - \frac{B}{(t + C)} \qquad (51)$$

Combining the foregoing expressions and solving for c, we obtain expression (52).

$$c = c_g \frac{RTc_{H_2O}}{p_{\text{neat}}} \qquad (52)$$

Upon substitution of the quantities for the case of *t*-butanol ($\log \gamma = 3.31$, $c_w = 1 \times 10^{-3}$ mol dm^{-3}, $T = 298$ K, $A = 7.23$, $B = 1107$, $C = 172$), we obtain $c = 1.7 \times 10^{-2}$ mol dm^{-3} which is taken as an upper limit to the concentration of *t*-butanol in the boundary layer of the bubble before it enters its compressive phase. This implies a hydrophobic-enhancement factor of 17.

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