Acetonylperoxyl Radicals, $\text{CH}_3\text{COCH}_2\text{O}_2$: A Study on the γ -Radiolysis and Pulse Radiolysis of Acetone in Oxygenated Aqueous Solutions

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Hydroxyl radicals from the radiolysis of $\text{N}_2\text{O}/\text{O}_2$ (4:1)-saturated aqueous solutions of acetone ($10^{-3} \text{ mol dm}^{-3}$) react with the solute by H-abstraction thereby forming acetonyl radicals. As shown by pulse radiolysis, the acetonyl radicals rapidly add oxygen ($k = 3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) thereby forming acetonylperoxyl radicals which decay by second-order kinetics ($2k = 8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). Under steady-state radiolysis conditions (0.24 Gys^{-1}) the products (G values in parentheses) are methylglyoxal (2.5), hydroxyacetone (0.5), formaldehyde (1.6), acids (1.7), carbon dioxide (0.5), organic (hydro)peroxides (0.4), hydrogen peroxide (2.2), and G(oxygen uptake) has been determined at 5.2. In the decay of the acetonylperoxyl radicals the major process (slightly less than one half) leads in a concerted reaction to two molecules of methylglyoxal and one molecule of hydrogen peroxide. The Russell mechanism which yields one molecule of methylglyoxal, hydroxyacetone and oxygen contributes about one fifth as does the breakdown into two molecules of formaldehyde, one molecule of oxygen and two acetyl radicals. Carbon dioxide, formaldehyde and acetic acid are among the products which result from the acetylperoxyl radicals formed upon oxygen addition to the acetyl radicals. About one tenth of the organic peroxyl radicals is converted into hydroperoxides by O_2^- produced as a byproduct in the water radiolysis.

Introduction

It has been reported that the radicals formed by the addition of OH radicals to the 6-position of pyrimidines do not react easily with oxygen, at least not in the presence of an electron donor such as N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD) [1]. Product studies carried out at the low dose rates of ^{60}Co γ -radiolysis indicated, however, that such radicals must react with oxygen [2]. Since the question of whether such radicals are reactive towards oxygen or not is of interest in the radiation chemical aspects of radiobiology (for a review see Ref. [3]), it was decided to carry out a detailed study on a model system. The C(6) OH-adduct radicals to uracil are β -oxoalkyl radicals which are well represented by the acetonyl radicals. Both have oxidizing properties due to a considerable contribution of the mesomeric structure with the free spin at oxygen. Hence it is not, a priori, obvious that they must react with oxygen at a near to diffusion-controlled rate

($k \approx 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) as practically all carbon-centred radicals do (*cf.* Ref. [4]).

The present paper continues the sequence of investigations into the fate of peroxyl radicals in aqueous solutions (*cf.* Ref. [5, 6] and references cited therein).

In aqueous solutions peroxyl radicals are most conveniently generated by ionizing radiation. In the radiolysis of water saturated with $\text{N}_2\text{O}/\text{O}_2$ (4:1 v/v) OH radicals, solvated electrons (e_{aq}^-) and some H atoms are formed (reaction (1)). The solvated electrons are then converted into OH radicals by N_2O (reaction (2)).

The OH radicals react with acetone by hydrogen abstraction (reaction (3); $k(3) = 9 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [7]).

At the acetone concentrations used the reaction of the H atom with acetone is too slow to compete with the scavenging by oxygen (reaction (4)).

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The $\text{HO}_2^\cdot$ radical has a pK_a value of 4.7 [8] and is fully dissociated in neutral and basic solutions. As will be shown, oxygen reacts with the acetonyl radicals converting them into the corresponding peroxy radicals (reaction (5)).

Thus the present system consists primarily of acetonylperoxyl radicals ($G^* = 5.2$, *cf.* [9]) and only 10% superoxide radicals ($G = 0.55$).

The present study reports the products and the decay kinetics of these peroxy radicals.

Experimental

Acetone was purified by fractional distillation to a purity of 99.9% (GC). Unless otherwise stated, solutions (10^{-3} – 10^{-1} mol dm $^{-3}$) were prepared by adding appropriate amounts of acetone to triply distilled water which had been presaturated with $\text{N}_2\text{O}/\text{O}_2$ (4:1 v/v). Irradiations were carried out at room temperature in a Co-60- γ source at a dose rate of 0.24 Gys $^{-1}$. The absorbed doses ranged between 57 and 230 Gy, *i.e.* the conversion was kept below 13%. Formaldehyde was determined by the acetylacetone method [10]. The determination of hydroxyacetone and methyl glyoxal was also based on the determination of formaldehyde, after periodate cleavage or reduction with NaBH_4 followed by periodate cleavage, respectively.

Total acids were determined by potentiometric titration against 0.01 mol dm $^{-3}$ NaOH. The presence of acetic acid as the major acidic product was confirmed by high-performance ion chromatography (Dionex ion chromatograph model 2020i; HPIC anion S4 separator with cation-hollow fibre suppressor; eluent 10^{-4} mol dm $^{-3}$ NaHCO_3).

Total (hydro)peroxide was determined iodometrically according to Allen *et al.* [11]. Organic hydroperoxides were determined by the same assay after H_2O_2 had been decomposed by catalase.

Oxygen uptake was measured with an oxygen-sensitive electrode (Wiss. Techn. Werkstätten, Weilheim, Germany). Carbon dioxide yields were determined by gas chromatography (3 m Porapak N). Detection was by flame ionization after the carbon dioxide had been catalytically reduced to methane.

Pulse radiolysis was carried out using a 2.8 MeV van-de-Graaff electron generator. The electron pulses were of 0.4–2 μs duration with doses ranging

from 10 to 30 Gy. The optical detection technique and data processing procedure have been described previously [12]. Dosimetry was performed with N_2O -saturated 1×10^{-2} mol dm $^{-3}$ KSCN solutions taking ϵ (480 nm) = 7600 dm 3 mol $^{-1}$ cm $^{-1}$ and $G = 6.0$ for $(\text{SCN})_2^\cdot$ [13]. Conductivity changes were monitored by an AC-operated (applied voltage 40 V, frequency 10 MHz) two-cell bridge as described by Asmus and Janata [14]. Dosimetry for conductivity experiments was done with a methylchloride-saturated O_2 -free solution containing 0.1 mol dm $^{-3}$ *tert*-butanol for which $G(\text{HCl})$ was taken as 3.1 [15]. For product studies at high dose rates, a sequence of 1 μs electron pulses (2 Gy/pulse, 0.5 Hz) was given to the samples. The absorbed doses did not exceed 320 Gy.

Results and Discussion

1. Product analysis

According to our present knowledge of peroxy radical chemistry in aqueous solutions the major expected products of the acetonylperoxyl radicals are pyruvic aldehyde, hydroxyacetone, formaldehyde and acetic acid. The determination of formaldehyde is straightforward (see Experimental). The determination of hydroxyacetone and pyruvic aldehyde can also be based on a formaldehyde determination. Three sets of experiments have been done. (i) Determination of formaldehyde (**A**), (ii) periodate cleavage with subsequent formaldehyde determination (**B**) and (iii) reduction with NaBH_4 followed by periodate cleavage and formaldehyde determination (**C**). **A** measures radiolytically formed formaldehyde. **B** measures the sum of radiolytically formed formaldehyde and that formed by periodate cleavage of hydroxyacetone. Under the conditions of **C** the radiolytically formed formaldehyde is reduced to methanol, and the subsequent periodate cleavage yields formaldehyde from both hydroxyacetone and pyruvic aldehyde. It will also include the acetonylhydroperoxide ($\text{CH}_3\text{COCH}_2\text{OOH}$) which must be among the organic peroxidic material (*cf.* [16]). The yield of such compounds is, however, low and only a small contribution from this source is to be expected. The rate constant of OH radicals with acetone is rather low and its concentrations cannot be increased beyond 10^{-3} mol dm $^{-3}$, otherwise it would compete effectively with N_2O for the solvated electrons. Hence even at very low doses (*i.e.* low percentages of conversion) the products, all of which react much faster with OH than acetone itself, will

* The G value is defined as molecules formed per 100 eV of absorbed energy.

start to react with the OH radicals and hence the dose yield curves are bent (e.g. Fig. 1A). G values have been calculated by extrapolating G vs. dose curves to zero dose (e.g. Fig. 1B). They are compiled in Table I.

2. Pulse radiolysis

The reaction of OH radicals with acetone: In a pulse-irradiated N_2O -saturated $2 \times 10^{-3} \text{ mol dm}^{-3}$ acetone solution no acid formation could be detected by the conductivity method. This indicates that the reaction of OH radicals with acetone does not take place at the C=O function to give the oxyl radical

Table I. Products and their G values in the radiolysis of $10^{-3} \text{ mol dm}^{-3}$ aqueous solution of acetone saturated with $\text{N}_2\text{O}/\text{O}_2$ (4:1 v/v).

Product	γ -Radiolysis	Electron pulses
Methylglyoxal	2.5	2.8
Hydroxyacetone	0.5	n.d.
Formaldehyde	1.6	1.2
Acids	1.7	0.2 ^a
Organic (hydro)peroxide	0.4, 1.3 ^b	0.2
H_2O_2	2.2, 1.6 ^b	2.5
O_2 uptake	5.2	n.d.
CO_2	0.5	0.4 ^a

^a Determined from net conductivity change in pulse irradiated acetone solutions (see text); n.d. not determined; ^b $10^{-1} \text{ mol dm}^{-3}$ acetone, O_2 -saturated solutions.

Fig. 1. A. Dose-yield plots of some products in the γ -radiolysis of $10^{-3} \text{ mol dm}^{-3}$ acetone solutions saturated with $\text{N}_2\text{O}/\text{O}_2$ (4:1 v/v). 1. Formaldehyde, 2. Formaldehyde after periodate treatment (i.e. the sum of formaldehyde and hydroxyacetone), 3. Formaldehyde after reduction with NaBH_4 and subsequent treatment with periodate (i.e. the sum of methylglyoxal and hydroxyacetone). B. G values of the products given in Fig. 1A as a function of dose.

(reaction (6)) which would quickly undergo β -scission to give acetic acid and a methyl radical (reaction (7)).

We have thus confirmed that H-abstraction is indeed the only reaction of the OH radical with acetone (cf. reaction (3)).

The acetonyl radical: Since acetone reacts readily with e_{aq}^- ($k = 6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [17]) but slowly with OH radicals, in the pulse radiolysis of a N_2O -saturated ($2.8 \times 10^{-2} \text{ mol dm}^{-3}$, $k(2) = 9.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) acetone solution ($5 \times 10^{-3} \text{ mol dm}^{-3}$ at pH 6.5) the acetonyl radical, $\text{CH}_3\text{COCH}_2^\cdot$, is produced *via* reaction (3) only with $G = 4.9$. About 10% of e_{aq}^- are scavenged by acetone to give the 2-hydroxypropyl-(2) radical. Fig. 2 shows the transient absorption spectrum of the acetonyl radical taken $5 \mu\text{s}$ after the pulse ($\approx 15 \text{ Gy}$ per pulse). It has been corrected for the contribution of the 2-hydroxy-propyl-(2) radical and for the loss due to bimolecular decay ($\approx 6\%$). The rate constant of the bimolecular decay of the acetonyl radical determined at 300 nm is $2k = 1.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The acetonylperoxyl radical: In an $\text{N}_2\text{O}/\text{O}_2$ (4:1 v/v)-saturated acetone solution ($5 \times 10^{-3} \text{ mol dm}^{-3}$) a different transient absorption spectrum from that observed under oxygen-free conditions is obtained $5 \mu\text{s}$

Fig. 2. Transient absorption spectra of the acetonyl radical (circles) and the acetonylperoxyl radical (triangles) observed in the pulse-radiolysis of $5 \times 10^{-3} \text{ mol dm}^{-3}$ aqueous acetone solutions saturated with N_2O and $\text{N}_2\text{O}/\text{O}_2$ (4:1 v/v), respectively.

after the pulse. In the presence of oxygen the acetonyl radical adds oxygen (reaction (5)) to give the acetonylperoxyl radical ($G \approx 4.9$). The H atoms formed in low yields in reaction (1) are scavenged by oxygen leading to $\text{H}^+ + \text{O}_2^-$ ($G=0.55$). The 2-hydroxy-propyl-(2) radical formed by e_{aq}^- scavenging also adds oxygen thereby producing the corresponding peroxyl radical ($G \approx 0.3$). The contributions of the latter two radicals to the overall absorption have been corrected for in the calculation of the extinction coefficient of the acetonylperoxyl radical. The absorption spectrum of the acetonylperoxyl radical is also shown in Fig. 2. The bimolecular decay rate constant of the acetonylperoxyl radical has been determined at 300 nm to be $2k = 8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The rate constant of reaction (5) has been determined by monitoring the absorption buildup at 350 nm in a $10^{-2} \text{ mol dm}^{-3}$ acetone solution saturated with a gas mixture containing mostly N_2O with varying (small) amounts of oxygen. Under these conditions the reaction of OH radicals with acetone is sufficiently fast ($t_{1/2} < 1 \mu\text{s}$) not to interfere with the subsequent O_2 addition process. Also at 350 nm the absorption due to the α -hydroxy-2-propyl-

peroxyl radical ($G \approx 0.6$; from the reaction of e_{aq}^- with acetone and subsequent addition of O_2) is negligible. The pseudo-first-order rate constant thus measured was found to be directly proportional to the oxygen concentration in the solution ($(2.6\text{--}9.1) \times 10^{-5} \text{ mol dm}^{-3}$). From these data the bimolecular rate constant $k(5) = 3.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was calculated.

Oxidizing properties of the acetonyl radical and the acetonylperoxyl radical. β -Oxoalkyl radicals have been shown [1, 18, 19] to be strongly oxidizing towards N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD). In an Ar-saturated 0.1 mol dm^{-3} acetone solution containing $(0.2\text{--}1.8) \times 10^{-4} \text{ mol dm}^{-3}$ TMPD at pH=8.5, the absorption buildup of TMPD^+ has been monitored at 565 nm where TMPD^+ has an absorption maximum. Within $\approx 100 \mu\text{s}$ after the pulse ($\approx 3 \text{ Gy/pulse}$) a plateau value is reached which corresponds to $G(\text{TMPD}^+) \approx G(\text{OH})$ if the losses due to radical-radical reactions are taken into account. The observed first-order rate constant of the buildup at 565 nm is linearly dependent on the concentration of TMPD. From the slope of the plot of k_{obs} vs. $[\text{TMPD}]$ the second-order rate constant for the formation of TMPD^+ from the reaction of acetonyl radicals with TMPD is calculated as $k = 1.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This value is quite similar to the corresponding values obtained for other β -oxoalkyl radicals [18, 19].

The reaction of acetonylperoxyl radicals with TMPD has also been monitored at 565 nm in an O_2 -saturated 0.1 mol dm^{-3} acetone solution at pH 11 which was mixed with an Ar-saturated solution of TMPD (4.5×10^{-5} and $1.0 \times 10^{-4} \text{ mol dm}^{-3}$) shortly before each pulse. Under these conditions the reaction of e_{aq}^- with acetone leads to the instantaneous formation of O_2^- [20] which is unreactive towards TMPD [1]. The absorption buildup of TMPD^+ in this case reaches the plateau value only after 1 ms. With $10^{-4} \text{ mol dm}^{-3}$ TMPD $G(\text{TMPD}^+) = 2.7$ at the plateau is reached. Correcting for some bimolecular decay of the acetonylperoxyl radicals the rate constant of its reaction with TMPD was calculated to be $k \approx 6 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This rate constant is close to that determined for the reaction of the hydroxymethylperoxyl radical with TMPD (Steenken, private communication).

Formation of O_2^- . To determine the yield of O_2^- in the bimolecular decay of the acetonylperoxyl radicals $3 \times 10^{-4} \text{ mol dm}^{-3}$ tetranitromethane (TNM) was ad-

ded to $\text{N}_2\text{O}/\text{O}_2$ -saturated solution of acetone and the buildup of nitroform anion (NF^-) was followed at 350 nm. Within 10 μs after the pulse a fast absorption buildup was observed which is mostly due to the reaction of primary $\text{O}_2^\cdot$ with TNM [21] with a small contribution from the absorption of the acetonylperoxy radical at 350 nm. After this initial absorption buildup a slower buildup is observed with $2k \approx 5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The net yield of NF^- in this second process was $G=0.2$, which is attributed to the yield of $\text{O}_2^\cdot$ from the bimolecular decay of the acetonylperoxy radicals.

Pulse conductometric measurements. In pulse conductivity experiments carried out in $\text{N}_2\text{O}/\text{O}_2$ -saturated solutions of acetone ($2 \times 10^{-3} \text{ mol dm}^{-3}$, pH 6.5) there is an immediate conductivity increase with $G(\text{acid}) = 0.4$ which is attributed to the formation of $\text{H}^+/\text{O}_2^\cdot$ from the reaction of the primary H atoms with O_2 . Within 20 ms after the pulse this conductivity change decays to a lower and permanent level corresponding to the formation of a permanent acidic species with $G \approx 0.2$.

In $\text{N}_2\text{O}/\text{O}_2$ -saturated basic solutions of acetone (pH 9.5–11.3), the conductivity of the solution was observed to decrease in two kinetically distinguishable steps. A decrease of conductivity in basic solutions is normally the result of acid formation. The proton of the acid is then quickly neutralised by OH^- ($\lambda^\circ = 198 \text{ } \Omega^{-1} \text{ cm}^{-1} \text{ equiv}^{-1}$ at 25°C) leaving behind

the anion with much lower equivalent conductivity ($\lambda^\circ = 30\text{--}65 \text{ } \Omega^{-1} \text{ cm}^{-1} \text{ equiv}^{-1}$) than OH^- .

The first process is kinetically of second order, $2k \approx 8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (pH 10–11). The net conductivity change connected with this process increases with pH ($G(\text{“acid”}) = 0.7$ at pH 10.1, $G(\text{“acid”}) = 1.5$ at pH 11.0). Since a major product in the radiolysis of $\text{N}_2\text{O}/\text{O}_2$ -saturated solutions of acetone is methylglyoxal ($\text{pK}_a = 11.0$), the above conductivity change observed in basic solutions of acetone is attributed to the formation of methylglyoxal in the bimolecular decay of the peroxy radical of acetone. As the pH of the solution increases towards the pK_a value of methylglyoxal, more and more of this product becomes deprotonated and thus more OH^- is consumed.

Following the above second-order process is a slow conductivity decrease, the kinetics of which can be ascribed to the OH^- -induced hydrolysis of CO_2 (*cf.* Ref. [22]). The yield of CO_2 as given by the measured net change of conductivity at several pH values was $G = 0.44$.

3. Reaction mechanism

The acetonylperoxy radical will decay primarily by selftermination, since it is the only major radical species initially present in the system. In the following reaction scheme we have put together the various

plausible reaction paths for the decay of the acetylperoxy radical which lead to the observed products given in Table I.

It is generally accepted that the bimolecular self-termination of peroxy radicals takes place *via* the formation of an unstable tetroxide as intermediate (reaction (8), *e.g.* Ref. [23]), which can either decay into the various products or revert to the parent peroxy radicals (reaction (9)). The observed second order decay rate constant (both by monitoring the absorption decay of the acetylperoxy radicals as well as the conductivity change caused by the formation of methylglyoxal) of $2k \approx 8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ represents therefore the kinetics of the overall process.

The four decay routes (reactions (10)–(13)) of the tetroxide are well-known processes (*cf.* Ref. [24]). Reaction (10) (the so-called Russell mechanism, *cf.* Ref. [25]) leads to the formation of equal amounts of methylglyoxal and hydroxyacetone. Since the yield of hydroxyacetone ($G = 0.5$) is considerably lower than the yield of methylglyoxal ($G = 2.5$), the contribution of reaction (10) can only be minor ($\approx 20\%$) because only $G(\text{peroxy radicals}) = 1.0$ follow this route together with its free-radical equivalent (reaction (17)). The excess amount of methylglyoxal found can come from either the concerted reaction (11) or from its free-radical equivalent, the reaction sequence (13), (15) (*cf.* Ref. [16, 26] and references cited therein), and (18) (for a review see Ref. [27]). However, since only a negligible yield of $\text{O}_2^{\cdot -}$ has been detected by its reaction with tetranitromethane (see above), the free-radical reaction path can play only a very minor role. The major part of methylglyoxal ($G = 2.0\text{--}2.3$) has to be attributed to reaction (11). Thus 40–45% of the peroxy radicals take this route. This value might be an underestimate, since due to the low reactivity of acetone towards OH radicals and the much higher reactivity of the products, especially methylglyoxal, a further degradation to acidic products is to be expected (*cf.* the high yield of acidic products under steady state radiolysis conditions).

Alternatives to reaction (15) for the decay of the oxyl radical formed *via* reaction (13) are reactions (16) and (17) (which take place within the solvent cage) and the β -scission reaction (14). Reaction (14) leads to the formation of equivalent amounts of formaldehyde and the acetyl radical.

Recently it has been shown that fragmentation reactions of peroxy radicals do not necessarily have

free oxyl radicals as intermediates but that a concerted route as depicted in reaction (12) can play a dominant role [5]. In the present system we are unable to distinguish between these two routes, because independent information of the fate of the oxyl radical (*e.g.* $k(14)/k(15)$) is not available.

The acetyl radical formed in reactions (12) and (14) rapidly adds oxygen (reaction (19)) to give the acetylperoxy radical.

The acetyl radical and its peroxy radical are the major radical species produced by the reaction of OH radical with acetaldehyde in the absence and presence of oxygen, respectively, and are being investigated in more detail in a separate study [28]. Under pulse radiolysis conditions, the acetylperoxy radicals decay mainly by self-termination to the corresponding oxyl radicals which quickly undergo β -scission to form CO_2 and the methyl radical or by the corresponding concerted process (reaction (20)).

The major product of methyl radicals under oxygenated conditions is again formaldehyde [16]. Therefore about twice as much formaldehyde as CO_2 is expected to be formed in the reaction routes (12)/(14), followed by (19) and (20). We have indeed found a large excess of formaldehyde over CO_2 . As expected, there are other decay routes as well. The reaction of the acetylperoxy radical with the acetylperoxy radical can, for example, lead (*via* the Russell mechanism) to acetic acid. In pulse radiolysis experiments some permanent acid has been found, and in steady-state radiolysis acetic acid is the major acid formed. Judging from the formaldehyde yield at least 15% ($G = 0.8$) of the peroxy radical must undergo the fragmentation reactions (12) and (14).

The organic peroxidic material found may include both the peroxide formed in reaction (16) (the yield of which may be expected to be low [16]) as well as the hydroperoxide produced by the reaction of acetylperoxy radical with $\text{O}_2^{\cdot -}$ (reaction (21)) especially under steady-state radiolysis conditions where $\text{O}_2^{\cdot -}$ can build up to sufficiently high steady-state concentrations.

In O_2 -saturated $10^{-1} \text{ mol dm}^{-3}$ acetone solutions solvated electrons are mainly scavenged by acetone. The resulting ketyl radical rapidly reacts with oxygen and subsequently eliminates $\text{HO}_2^\cdot/\text{O}_2^\cdot$ [20]. Compared to $\text{N}_2\text{O}/\text{O}_2$ -saturated solutions the acetonylperoxyl radical yield is halved while $\text{O}_2^\cdot$ is now the most abundant species. Under such conditions 47% of the acetonylperoxyl radicals are converted into organic hydroperoxides, mainly by reaction (21) (see Table I).

Besides the acetonylperoxyl radical the acetylperoxyl radical may also react with $\text{O}_2^\cdot$. Reaction (22) depicts its conversion into peracetic acid.

Peracetic acid readily oxidizes aldehydes [29] (*e.g.* methylglyoxal) producing two equivalents of acid, thus possibly contributing to the acid formation in the steady-state radiolysis experiments. The organic peroxidic material is formed with a *G* value of about 0.4 which means that hydroperoxide formation makes up about 8% of the fate of the organic peroxyl radicals. On the whole the material balance falls

somewhat short and the values of the various contributions are lower limits (underestimates). The reasons for this are mentioned above. If one neglects the reactions of $\text{O}_2^\cdot$ one arrives at the following conclusions which are based on a reduced data set ($G(\text{methylglyoxal}) = 2.5$; $G(\text{hydroxyacetone}) = 0.5$; $G(\text{formaldehyde}) = 1.6$).

Conclusions

Like other carbon-centred radicals, acetonyl radicals rapidly add oxygen ($k = 3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) thereby forming acetonylperoxyl radicals. In aqueous solutions acetonylperoxyl radicals decay by second-order kinetics ($2k = 8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). About one half of the acetonylperoxyl radicals decay by a concerted reaction leading to two molecules of methylglyoxal and one molecule of hydrogen peroxide (reaction (11)). Second in importance (slightly more than one quarter) is the Russell mechanism (reaction (10)) which leads to one molecule of methylglyoxal, hydroxyacetone and oxygen. The fragmentation reaction (reactions (12) and (14)) which produces two molecules of formaldehyde, one molecule of oxygen and two acetyl radicals contributes slightly less than one quarter. Other reactions appear to be of minor importance, especially the 1,2-H-shift of intermediate oxyl radicals (reaction (15)) which in other peroxyl radical systems can be a predominating process (*cf.* Ref. [26]).

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