Radiolysis of the poly(acrylic acid) model 2,4-dimethylglutaric acid: a pulse radiolysis and product study

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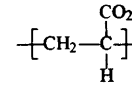
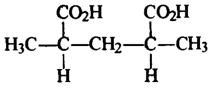
2,4-Dimethylglutaric acid† (2,4-DMGA), a low molecular weight model compound for poly(acrylic acid), reacts in aqueous solution with radiolytically generated hydroxyl radicals with $k = 9.5 \times 10^8$ (fully protonated form) and $k = 1.6 \times 10^9$ dm^3 mol^{-1} s^{-1} (doubly charged anion), as determined by pulse radiolysis. In deoxygenated solutions, the resulting 2,4-DMGA radicals decay bimolecularly ($2k = 4.0 \times 10^8$ dm^3 mol^{-1} s^{-1} at pH 3.2 and 1.3×10^7 dm^3 mol^{-1} s^{-1} at pH 10) by dimerisation and disproportionation (ratio 1:1.3 at pH 3.6). In N_2O–O_2-saturated solutions, 2,4-DMGA radicals react with oxygen ($k = 1.2 \times 10^9$ dm^3 mol^{-1} s^{-1} at pH 3.6). The decay of the peroxyl radicals ($2k = 7.1 \times 10^7$ dm^3 mol^{-1} s^{-1} at pH 3.6 and 2.6×10^6 dm^3 mol^{-1} s^{-1} at pH 10) leads to the formation of hydroxy- and carbonyl-containing as well as to C–C fragmentation and decarboxylation products, the major ones being (G values in units of 10^{-7} mol J^{-1} in parentheses): 2-methyl-4-oxovaleric acid (1.4), 2,4-dimethyl-3-oxoglutaric acid (0.75), acetylacetone (0.5), 2-formyl-4-methylglutaric acid (0.45), 2-hydroxymethyl-4-methylglutaric acid (0.2), 2- and 3-hydroxy-2,4-dimethylglutaric acid (0.2), 2-methylglutaraldehydic acid (0.2), 2-methylmalonaldehydic acid (0.2) and acetaldehyde (0.25). The formation of acetylacetone is of special interest, since a similar product is also formed in poly(acrylic acid) in relatively high yields. It is suggested to be induced by the peroxyl radical in the α-position to the carboxyl group (C^2–O_2^-) which abstracts intramolecularly the C^4–H. The rate constant for this intramolecular H-abstraction has been estimated at 0.5 s^{-1}. The hydroperoxide product formed in subsequent steps decomposes into acetylacetone. The other products listed are explained on the basis of known peroxyl radical reactions.

Poly(acrylic acid), PAA, is of considerable practical importance as an additive in hydraulic fluids and petroleum recovery liquids, as an ion-exchange resin where a weak acid is desired, as a suspending or flocculating agent, as a thickener for cosmetics and an adhesive.[1] There is also a growing interest in the biomedical use of PAA, either pure or as a copolymer, grafted material, composite or polyelectrolyte complex. These applications include, for example, high-performance dental cements,[1,2] composites for endosteal implants,[3] contractile membrane materials and thromboresistant surfaces.[4] Owing to their ability to respond to stimuli such as pH, ionic strength or electric field,[5] hydrogels of PAA and its copolymers are studied for their potential applications in biomedical devices, *e.g.* as pore-size controlling agents in the membrane of an artificial pancreas. The most convenient method for hydrogel formation and sterilization of polymeric biomaterials is the treatment of the polymers with ionizing radiation in aqueous solution (*e.g.* refs. 6 and 7). The effects of ionizing radiation on PAA have been studied in some detail.[8–14] Valuable information as to the primary reactions involved in the radical chemistry of PAA and its low molecular weight analogues have been obtained by EPR spectroscopy.[15,16] In our recent studies on the OH-radical-induced reactions of PAA[13,14] it became apparent that some of the features observed with the polymer should be studied at the low molecular weight level. Under such conditions, product studies can be carried out which are as yet impossible with the polymer. As a model system we have chosen 2,4-dimethylglutaric acid, 2,4-DMGA.



$$\left[CH_2-\overset{CO_2H}{\underset{H}{C}}\right]_n$$

PAA



$$H_3C-\overset{CO_2H}{\underset{H}{C}}-CH_2-\overset{CO_2H}{\underset{H}{C}}-CH_3$$

2,4-DMGA

This compound resembles PAA in so far as it has the same structural subunits: a methylene group and, adjacent to this, a methine group which carries the carboxy group. The two methyl groups in 2,4-DMGA are not expected to introduce drastic changes in the free-radical chemistry compared to PAA.

Experimental

2,4-Dimethylglutaric acid (2,4-DMGA, Aldrich and Janssen), a mixture of D, L and *meso* forms, was used as received. Its purity was confirmed by gas chromatography (after trimethylsilylation) and ion chromatography. The pK_a values of 2,4-DMGA were estimated by titration.

Solutions were made in Milli-Q-purified (Millipore) water; the pH was adjusted with $HClO_4$ or NaOH. Prior to irradiation, solutions were saturated with N_2O (purified with an Oxisorb column; Messer-Griesheim) or with N_2O–O_2 (4:1 v/v) (Messer-Griesheim).

γ-Irradiations were carried out in a ^{137}Cs source (Oris IBL 437 C) at a dose rate of 0.17 Gy s^{-1} or in a panorama ^{60}Co source (Nuclear Engineering) at a dose rate of 0.12 Gy s^{-1}.

Irradiation products were analysed by gas chromatography (GC) and gas chromatography with mass spectrometry (GC–MS) after derivatization with *N*,*N*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA, Macherey Nagel) or *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA,

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† 2,4-Dimethylglutaric acid = 2,4-dimethylpentanedioic acid.

Table 1 Products and their G values of 2,4-DMGA (10^{-3} mol dm^{-3}) in N_2O- and N_2O–O_2-saturated aqueous solutions at pH 3.6

	$G/10^{-7}$ mol J^{-1}	
Products	N_2O	N_2O–O_2
Unsaturated acids (**4** + **5**)	1.4	absent
Dimers **6**	1.1	absent
2-Formyl-4-methylglutaric acid **14**	absent	0.4–0.5
2,4-Dimethyl-3-oxoglutaric acid **15**	absent	0.75
2-Hydroxymethyl-4-methylglutaric acid **16**	absent	0.2
2- and 3-Hydroxy-2,4-dimethylglutaric acid (**17** + **18**)	absent	0.2
2-Methyl-4-oxovaleric acid **13**	absent	1.4
2-Methylglutaraldehydic acid	absent	0.2
5-Hydroxy-2-methyl-4-oxovaleric acid	absent	0.15
Acetylacetone **24**	absent	0.5
Unidentified products containing 7 carbons	absent	0.25
2-Methylmalonaldehydic acid **27**	absent	0.2
2-Oxopropionic acid	absent	< 0.1
Acetaldehyde	*a*	0.25
Formaldehyde	*a*	0.1
Minor unidentified fragment products	absent	0.4
Carbon dioxide	*a*	2.6
Hydrogen peroxide	*a*	1.9
Organic hydroperoxides	*a*	0.3

[a] Not determined.

Fluka). For the conversion of carbonyl groups into the corresponding alcohols, samples were reduced with $NaBH_4$ prior to trimethylsilylation. Samples irradiated at high pH were converted into the free acids by passing the solution through Amberlite IR-120 P ion exchange resin (Sigma) prior to rotary evaporation and derivation. For the GC analyses (Varian 3700) of BSTFA-derivatized samples, a 25 m FS-345,5 column was operated at 50–280 °C, 6 °C min^{-1}; PFBHA-derivatives were analysed on a 25 m SE-54 column operated at 50–250 °C, 8 °C min^{-1} or on a 20 m SE-54 column operated at 50–270 °C, 6 °C min^{-1}. Hydrogen was used as the carrier gas. GC–MS analyses (Hewlett-Packard 5890-II with an HP 5971A Mass Selective Detector) were carried out using a 12 m HP-Ultra-1 (cross-linked silicone gum) column (operated at 80–270 °C, 6 °C min^{-1} or, for separation of the unsaturated acids, at 80–93 °C, 0.5 °C min^{-1}; above 93 °C, 0.1 °C min^{-1} and, for better resolution of the dimers, at 80–200 °C, 6 °C min^{-1}, 200–250 °C, 3 °C min^{-1}). Irradiation products were identified by the mass spectra of their trimethylsilyl derivatives; *m/z* 4-carboxy-2-methylpent-4-enoic acid and 4-carboxy-2-methylpent-2-enoic acid **4** + **5** (2 TMS, MW = 302): 302 (< 1%), 287 (14), 258 (24), 231 (27), 147 (59), 96 (84), 95 (5), 75 (32) and 73 (100); and 302 (2%), 287 (27), 229 (16), 196 (12), 184 (45), 169 (48), 147 (73), 95 (37), 75 (55) and 73 (100). Dimers **6** (a selected typical spectrum) (4 TMS, MW = 606): 591 (7%), 371 (4), 304 (9), 303 (10), 281 (9), 231 (12), 218 (48), 213 (23), 186 (22), 147 (37), 143 (20), 130 (25), 75 (21) and 73 (100). 2,4-Dimethyl-3-oxoglutaric acid **15** (enolic form, 3 TMS, MW = 390): 390 (2%), 375 (17), 300 (9), 272 (40), 257 (15), 245 (7), 167 (21), 147 (29), 130 (7) and 73 (100). 2-Hydroxymethyl-4-methylglutaric acid **16** (3 TMS, MW = 392): 377 (18%), 302 (4), 287 (7), 243 (4), 233 (3), 217 (18), 185 (13), 169 (16), 149 (15), 147 (46), 133 (14), 129 (20), 103 (10), 95 (25), 75 (27) and 73 (100). 2- and 3-Hydroxy-2,4-dimethylglutaric acid **17** + **18** (a selected typical spectrum) (3 TMS, MW = 392): 377 (5%), 287 (5), 247 (16), 231 (9), 218 (19), 203 (14), 185 (7), 147 (42), 133 (10), 115 (20), 75 (22) and 73 (100). 2-Methyl-4-oxovaleric acid **13** (1 TMS, MW = 202): 202 (1%), 187 (34), 159 (58), 143 (33), 129 (14), 75 (100) and 73 (73), detected also in enolic form (2 TMS, MW = 274): 274 (3%), 259 (100), 245 (7), 184 (12), 169 (6), 157 (8), 147 (76), 133 (8), 127 (7), 113 (9), 83 (20) and 73 (75) and after reduction as 2-methyl-4-hydroxyvaleric acid (2 TMS, MW = 276): 261 (21%), 232 (16), 217 (7), 203 (5), 171 (42), 147 (62), 143 (27), 133 (9), 117 (69), 75 (84) and 73 (100). 2-Methylglutaraldehydic acid detected only after reduction as 2-methyl-5-hydroxyvaleric acid (2 TMS, MW = 276): 276 (< 1%), 261 (23), 203 (3), 186 (18), 171 (16), 147 (100), 133 (11), 129 (9), 117 (6), 103 (9), 101 (9), 75 (52) and 73 (76). 2-Methylmalonaldehydic acid **27** only detected after reduction as 2-methyl-3-hydroxypropionic acid (2 TMS, MW = 248): 233 (18%), 128 (4), 177 (9), 147 (100), 143 (7), 133 (7), 103 (9), 75 (21) and 73 (43).

Since the reference material for the majority of analysed products was not available, for quantitation the response factors have been estimated by assuming equal mass response for non-derivatized products as for non-derivatized substrate. This simplification may lead in some cases to an error of up to 20%.

Acetylacetone was identified by GC in the form of its PFBHA derivative by comparison with authentic material (Aldrich). Quantitation was performed by UV measurements making use of the strong absorbance of its enolate form in alkaline solutions ($\varepsilon_{294\ nm} = 2.14 \times 10^4$ dm^3 mol^{-1} cm^{-1}).[17]

For the detection of monocarboxylic acids and to follow the consumption of 2,4-DMGA, high performance ion chromatography was used (Dionex 2010i, IonPac AS9-SC column, eluent: 5×10^{-4} mol dm^{-3} $NaHCO_3$ and 1.8×10^{-3} mol dm^{-3} Na_2CO_3 + 1.7×10^{-3} mol dm^{-3}, respectively). Carbon dioxide was determined as carbonate with the IonPac HPICE AS-1 column using water as eluent (in the absence of suppressor).

Carbonyl-containing compounds were derivatized with 2,4-dinitrophenylhydrazine[18] and the absorbance of the resulting hydrazones was measured in alkaline methanol solution at 430 nm. Owing to their instability the absorbances were extrapolated to 'zero time', *i.e.* to the time of adding the base solution to the sample.[19,20] An average absorption coefficient of 2.3×10^4 dm^3 mol^{-1} cm^{-1} was assumed. The total of the carbonyl yield as determined by this assay [G(total carbonyl) $\approx 4.3 \times 10^{-7}$ mol J^{-1}], which compares well with the yields of such compounds determined by GC ($G \approx 4.6 \times 10^{-7}$ mol J^{-1}; *cf.* Table 1), allows us to infer that not much material has escaped our attention.

The yield of H_2O_2 and organic hydroperoxides was determined by Allen's reagent[21] modified by the addition of *ca.* 1×10^{-3} mol dm^{-3} of *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine dihydrochloride (TMPD). Under such conditions the iodine formed reacts fast and quantitatively with TMPD yielding the relatively stable TMPD radical cation ($\varepsilon_{565\ nm}$ = 1.25×10^4 dm^3 mol^{-1} cm^{-1}).[22] This modified method prevents iodine loss otherwise observed in our system (possibly owing to its reaction with α-oxomethylene compounds, *i.e.* an iodoform-type reaction). As for Allen's reagent, the absorbance resulting from the H_2O_2 reaction builds up in less than a minute, while the slow increase in the 15–30 min time range is attributed to the reduction of organic hydroperoxides. The deoxygenated TMPD–Allen's reagent had to be prepared fresh before each analysis since TMPD undergoes a relatively fast autoxidation. Blanks were analysed in the same way.

Pulse radiolysis experiments were performed with a 2.8 MeV van de Graaf accelerator generating electron pulses of 0.4–4 μs duration.[23] Dosimetry was performed with thiocyanate solutions.

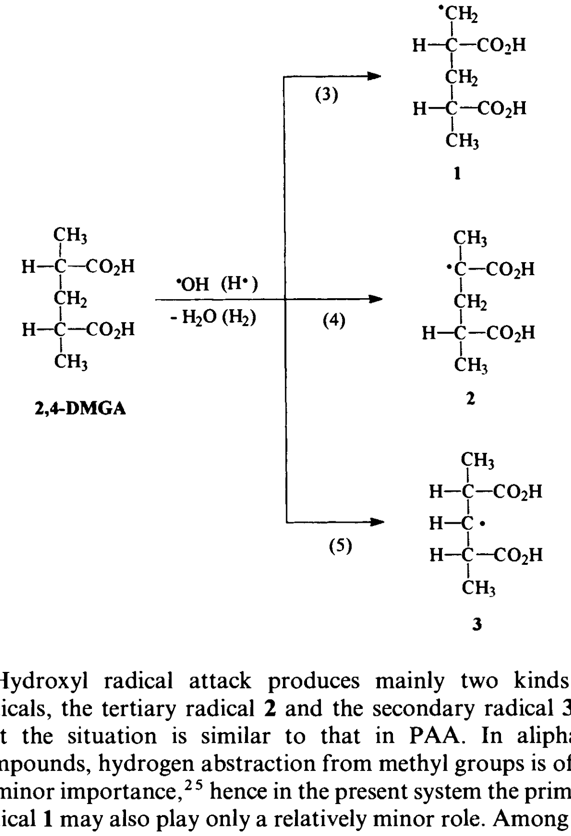
Results and discussion

Anoxic conditions

In dilute deoxygenated aqueous solutions of 2,4-DMGA (10^{-3} mol dm^{-3}) the ionizing radiation is absorbed mainly by water. Interaction of radiation with water leads to the formation of reactive species $^{\bullet}OH$, $^{\bullet}H$ and e^-_{aq} [reaction (1)]. In N_2O-saturated solutions, solvated electrons are converted into further hydroxyl radicals [reaction (2)]. Under these conditions the radiation chemical yields are $G(^{\bullet}OH) = 5.6 \times 10^{-7}$ mol J^{-1} and $G(H^{\bullet}) = 0.6 \times 10^{-7}$ mol J^{-1}.[24] These radicals react with 2,4-DMGA by hydrogen abstraction leading to the formation of three types of alkyl radicals **1**, **2** and **3** localized at the α- and β-positions to the carboxylic group [reactions (3)–(5)].

$$H_2O \xrightarrow{\text{ionizing radiation}} {}^{\bullet}OH, e_{aq}, H^{\bullet}, H^+, H_2, H_2O_2 \quad (1)$$

$$N_2O + e_{aq} \longrightarrow {}^{\bullet}OH + OH^- + N_2 \quad (2)$$



Hydroxyl radical attack produces mainly two kinds of radicals, the tertiary radical **2** and the secondary radical **3** so that the situation is similar to that in PAA. In aliphatic compounds, hydrogen abstraction from methyl groups is often of minor importance,[25] hence in the present system the primary radical **1** may also play only a relatively minor role. Among the products formed in the presence of O_2 (see below) 2-formyl-4-methylglutaric acid **14** and 2-hydroxymethyl-4-methylglutaric acid **16** must have radical **1** as precursor. The material balance under these conditions is not complete, but from the *G* values of **14** and **16** it seems that the yield of radical **1** is less than 20%. In any case, it would undergo similar reactions to radical **3**. In the case of the acetate ion it has been shown that OH radicals do not react with the carboxylate function,[26] in good agreement with the conclusions arrived at in earlier studies on the radiolysis of low molecular weight carboxylic acids.[27,28] Hence also for the present system, this reaction can be neglected.

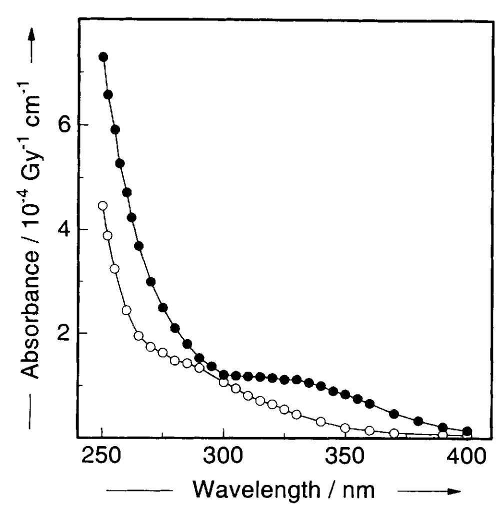


Fig. 1 Absorption spectra of the 2,4-DMGA-derived radicals recorded in N_2O-saturated 1×10^{-3} mol dm^{-3} 2,4-DMGA solution, 6–10 μs after a 45 Gy pulse at pH 3.6 (○) and pH 10 (●). Values were corrected for some 10% OH-radical loss owing to bimolecular self-termination.

The rate constants for the reactions of OH radicals with 2,4-DMGA (pK_a values at 4.2 and 5.3, *cf.* ref. 29 for similar acids) were determined at pH 3.0 ($k = 9.5 \times 10^8$ dm^3 mol^{-1} s^{-1}; fully protonated 2,4-DMGA) and 9.2 ($k = 1.6 \times 10^9$ dm^3 mol^{-1} s^{-1}; fully deprotonated 2,4-DMGA) using the thiocyanate competition technique.[30] It is typical for carboxylic acids that their anions react faster with the OH radical than the fully protonated acids[30] and an effect of similar magnitude has been found in the case of PAA.[12] The rate constants measured in this study are compiled in Table 2.

Absorption spectra of 2,4-DMGA radicals have no maxima in the range $\lambda > 250$ nm and show decreasing absorbance towards longer wavelengths (Fig. 1). In acidic and alkaline solutions the spectra consist of two components: a main band with a maximum below 250 nm and a shoulder at *ca.* 290 nm at pH 3.6 and at *ca.* 330 nm at pH 10. This feature is attributed to the existence of two different radicals, *i.e.* the ones localized in the α- and the β-position to the carboxylic group. For simple carboxylic acids the β-radicals are known to have the absorbance maximum below 250 nm and we therefore assume that in the present system they contribute to the main absorption band only. The α-radicals of monocarboxylic acids, such as propionic or butyric acid, exhibit a second absorption band at longer wavelength.[27] The position of its maximum depends on the state of protonation of the carboxylic group in a similar way as the position of the shoulder observed in the spectra of 2,4-DMGA radicals. Spectra similar to ours, with a shoulder rather than a well-developed maximum at longer wavelength typical for α-radicals of monocarboxylic acids, have been reported for the radicals derived from succinic and tricarballylic acid (propane-1,2,3-tricarboxylic acid).[31] Hence in our system as well, the α-radicals will contribute not only to the absorption in the shoulder region, but also to the main absorption band and at shorter wavelength. Note that the initial absorption spectra of the PAA-derived radicals resemble closely the 2,4-DMGA-derived ones.[13]

One can expect that OH radicals, owing to their electrophilic properties, could exibit some selectivity in the attack on α- and β-positions, an effect that is quite strong in the case of the OH radical reaction with alcohols, both those of low molecular

Table 2 Rate constants of the reactions of OH radicals with 2,4-DMGA and the subsequent reactions of the 2,4-DMGA-derived radicals

Reaction	Free acid	Dianion
$^{\bullet}OH$ + 2,4-DMGA	9.5×10^8 dm^3 mol^{-1} s^{-1}	1.6×10^9 dm^3 mol^{-1} s^{-1}
$R^{\bullet} + R^{\bullet}$	4.0×10^8 dm^3 mol^{-1} s^{-1}	1.3×10^7 dm^3 mol^{-1} s^{-1}
$R^{\bullet} + O_2$	1.2×10^9 dm^3 mol^{-1} s^{-1}	1.0×10^9 dm^3 mol^{-1} s^{-1}
$ROO^{\bullet} + ROO^{\bullet}$	7.1×10^7 dm^3 mol^{-1} s^{-1}	2.6×10^6 dm^3 mol^{-1} s^{-1}
$ROO^{\bullet}$ (intramolecular H-transfer)	≈ 0.5 s^{-1}	

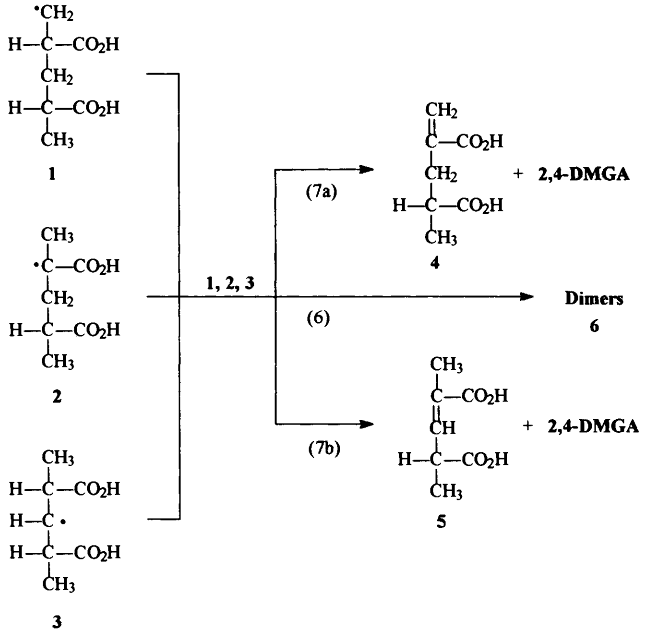
weight[25] and polymeric.[32] However, in monocarboxylic acids a preference for attacking the α-position is less pronounced[27] and is also affected by the state of protonation of carboxylic groups, *e.g.* in the case of propionic acid the fraction of OH radicals attacking the α-position has been estimated to increase from 35% at pH 3 to 55% at pH 10.[27] An exact measurement of the proportion between α- and β-radicals formed in our system is difficult. The method of selective oxidation by tetranitromethane, used for this purpose in the case of alcohols,[25,32] cannot be applied in the present system, since the α-radicals formed in the present system are less reducing than α-hydroxyalkyl radicals. However, some information can be obtained from the product analysis performed on 2,4-DMGA irradiated in oxygenated solutions (for details see below): the combined yields of 2-methyl-4-oxovaleric acid **13** and acetylacetone **24** which must have the radicals at the α-position as precursor is 34% of the total 2,4-DMGA radical yield in N_2O–O_2-saturated solution at pH 3.6. At pH 10 this value rises to 42%. These values have to be considered as lower limits of the yield of α-radicals, since further (minor) products may also have these radicals as precursors.

The kinetics of the decay of the 2,4-DMGA radicals were followed at 265 nm. The major part of radicals decayed according to second-order kinetics. However, a slower component involving *ca.* 10% of the absorption was observed at both pH values. The rate constant, calculated for the major decay, depends on the state of protonation of the carboxylic groups. At pH 3.2 it is equal to $2k = 4 \times 10^8$ dm^3 mol^{-1} s^{-1}, but when both carboxylic groups are dissociated (pH 10.0) it drops to $2k = 1.3 \times 10^7$ dm^3 mol^{-1} s^{-1}. This pronounced pH dependence is due to the fact that at high pH two doubly charged radicals have to react with one another. An even stronger effect of the state of protonation is observed in the case of PAA derived radicals, where at high pH the strong repulsive forces between the negatively charged polymer chains slow down the bimolecular decay of the macroradicals to such an extent that its first half-life is now in the order of 20 min.[33]

The non-uniform decay may be attributed to some differences between the individual rate constants of the termination reactions of radicals **1**, **2** and **3**. It may be possible that the primary and secondary radicals **1** and **3** react faster with one another and are more quickly depopulated, while some of the tertiary radicals **2** remain and react with each other with a lower rate constant.

Almost no residual absorbance at $\lambda > 250$ nm has been found after γ- or pulse-irradiation. This is expected since the majority of stable products are unsaturated acids and dimers containing no chromophores absorbing at long wavelengths [reactions (6) and (7)].

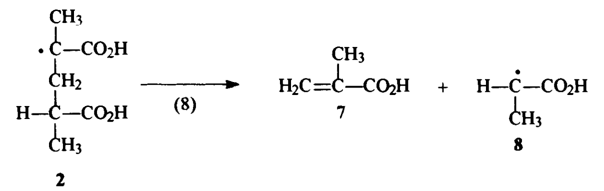
Evidence for reactions (6) and (7) has been obtained from product studies. Radiolysis of 2,4-DMGA in deoxygenated solution at the natural pH of 3.6 results in the formation of alkenic products and dimers. Three isomeric unsaturated acids have been found by GC–MS, corresponding to the *cis* and *trans* isomers of 4-carboxy-2-methylpent-2-enoic acid **5** and 4-carboxy-2-methylpent-4-enoic acid **4**. At pH 3.6, this combined initial yield, extrapolated to zero dose, is $G(\mathbf{4} + \mathbf{5}) = 1.4 \times 10^{-7}$ mol J^{-1}. As expected, the yield of unsaturated acids is not linear with dose at the substrate concentration used. This



is attributed to the fact that the unsaturated acids react with OH radicals considerably faster than the substrate [*cf.* $k(^{\bullet}OH$ + acrylic acid) $= 1.5 \times 10^9$ dm^3 mol^{-1} s^{-1}, $k(^{\bullet}OH$ + propionic acid) $= 4.5 \times 10^8$ dm^3 mol^{-1} s^{-1}][30] and OH-substituted 2,4-dimethylglutaric acids (that should be among the final products of the reaction of OH radicals with these unsaturated acids) have indeed been detected at elevated doses.

At least eight isomeric dimers are formed in reaction (6) (gas chromatogram not shown). This large number of different dimers results from the six possible crosslink sitings and up to four chiral centres present in these compounds. Despite the fact that the dimers, when substituted by four trimethylsilyl groups, have relatively high molecular weight and cannot be determined by GC under our conditions with high accuracy (loss of some material occurs), we can estimate their yield from the high-dose data to be in the order of $G(\text{dimers}) = 1.1 \times 10^{-7}$ mol J^{-1} at pH 3.6. Since two radicals react to form one unsaturated acid or one dimer [reactions (6) and (7)], the total yield of radicals involved in these two processes is *ca.* 5×10^{-7} mol J^{-1}. This indicates that disproportionation and combination are the major reaction pathways of 2,4-DMGA-derived radicals. Monocarboxylic acids were not detected indicating that fragmentation reactions [such as reaction (8)] must be of minor importance under these conditions. At the dose rate of our experiments and at pH 3.2 the radicals have a lifetime of 0.17 s and slightly longer at pH 10 (0.94 s). Reactions such as (8) must therefore be much slower than these values. It is worth mentioning that in the case of PAA-derived radicals at pH 10, where these radicals have a very long life-time, chain scission [similar to fragmentation reaction (8) in the present case] indeed occurs and that it proceeds with half-lives of *ca.* 20–30 s.[13,33]

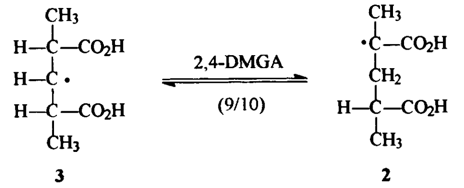
Considering that upon the formation of the unsaturated acids one molecule of 2,4-DMGA is regenerated [*cf.* reaction (7)]



G(2,4-DMGA consumption) = 3.9×10^{-7} mol J^{-1} is in good agreement with the G values of dimers and unsaturated acids.

Product analysis also provides evidence that the proportion between disproportionation and combination is influenced by the state of protonation of carboxylic groups. When 2,4-DMGA is irradiated at pH 10 G(unsaturated acids) increases to 2.1×10^{-7} mol J^{-1}, while the yield of dimers is reduced to $G = 0.6 \times 10^{-7}$ mol J^{-1}. This may be due to some extent to an increase in the fraction of α-radicals at high pH. Since the α-radicals have more hydrogen atoms at the neighbouring carbon atoms than the β-radicals, they are expected to be more prone to disproportionation.

In the radiolysis of PAA there is strong evidence that the radicals of type **3** may be converted into radicals of type **2**.[13,14]



In PAA this is favoured by the long lifetime of the polymer radicals and the fact that it can occur as an intramolecular reaction. In the case of low molecular weight carboxylic acids, the conversion of β-radicals into α-radicals has been observed at very high carboxylic acid concentrations and since its rate depends on the carboxylic acid concentration, it must proceed intermolecularly by H-abstaction, rather than intramolecularly by a 1,2-H shift.[16] At the dose rates of the present experiments and the low 2,4-DMGA concentration used, reaction (9) can hence only be of little importance.

Oxygenated solutions

In the case of PAA a detailed product analysis is not possible. However, there was, for example, the interesting observation that acetylacetone-like material seems to be a major reaction product of the PAA-derived radicals in oxygenated solutions.[13] Also, the present model system is complex (three different primary radical species have to be considered), and hence it is not feasible to give a complete reaction scheme, but the data will permit at least some idea regarding the major pathways in this system. On this basis, suggestions can be made as to the potential reactions in the polymer system, *e.g.* fragmentation and decarboxylation reactions.

In irradiated 2,4-DMGA solutions saturated with N_2O–O_2, O_2 reacts with the radicals **1**–**3** yielding the peroxyl radicals **9**–**11** [reactions (11)–(13)].

The overall rates of O_2 addition were investigated by following the initial increase in absorbance of peroxyl radicals at 300 nm. The rate constants (Table 2) are close to diffusion-controlled and thus similar to the values observed for the majority of carbon-centred radicals.[34]

The overall absorption spectra of the 2,4-DMGA-derived peroxyl radicals have no maxima at $\lambda > 250$ nm (Fig. 2). Some 10% of the radicals are $HO_2^{\bullet}/O_2^{\bullet -}$ resulting from the scavenging of the H atoms by O_2. When the spectra are corrected for their contribution (*cf.* ref. 35) there is no noticeable difference between the spectra at pH 3.6 and 10 (inset in Fig. 2). It is known that the α-peroxyl radicals of carboxylic acids are much more acidic than their parent compounds[36] and it is likely that the α-carboxylate group of **10** remains deprotonated even at the low pH.

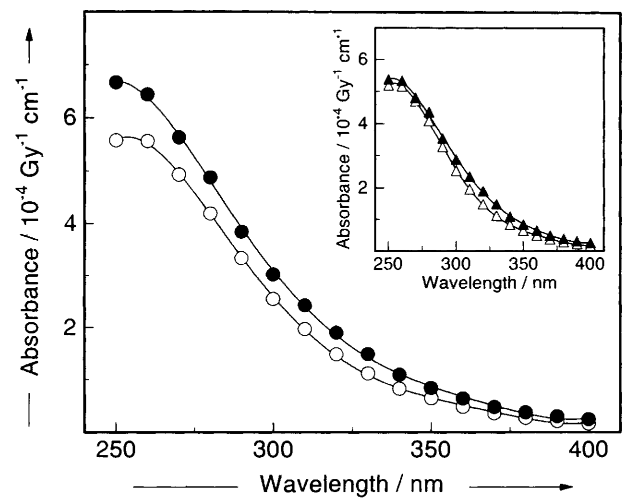
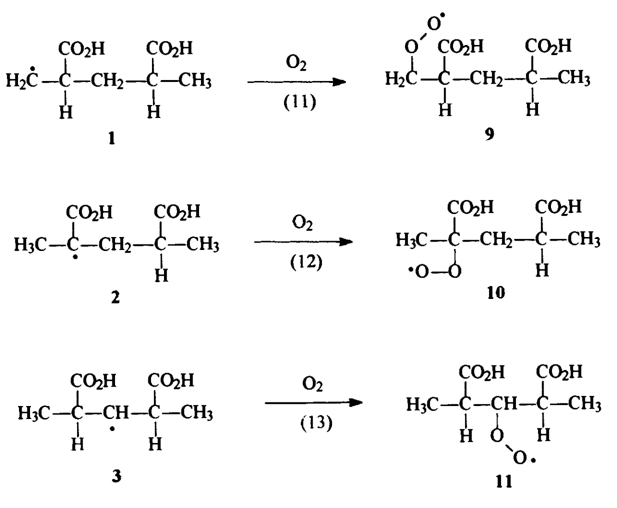


Fig. 2 Absorption spectra of the 2,4-DMGA-derived peroxyl radicals recorded in N_2O–O_2-saturated 1×10^{-3} mol dm^{-3} 2,4-DMGA solution, 30–80 μs after a pulse of 8 Gy, at pH 3.6 (○) and pH 10 (●). Inset: spectra at pH 3.6 (△) and pH 10 (▲) corrected for the absorbance of $HO_2^{\bullet}/O_2^{\bullet -}$.

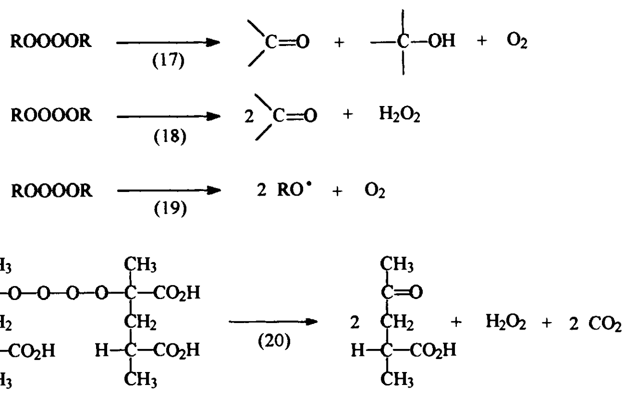


The decay of 2,4-DMGA-derived peroxyl radicals (measured at 300 nm) follows second-order kinetics. The overall rate constants are $2k = 7.1 \times 10^7$ dm^3 mol^{-1} s^{-1} at pH 3.6 and $2k = 2.6 \times 10^6$ dm^3 mol^{-1} s^{-1} at pH 10. A pH effect of a similar magnitude has been observed in the case of the carbon-centred radicals **1**–**3** (see above).

The yields of the identified products are given in Table 1. The material balance is reasonable, indicating that not much material appears to have escaped our attention. These data refer to the γ-irradiation of 1×10^{-3} mol dm^{-3} 2,4-DMGA solution at natural pH, *i.e.* 3.6. Irradiation of 2,4-DMGA at pH 10 leads to some changes in the proportions between product yields. For example, the yield of acetylacetone **24** increases to $G = 0.95 \times 10^{-7}$ mol J^{-1}, while G(2,4-dimethyl-3-oxoglutaric acid **15**) decreases to a value of 0.2×10^{-7} mol J^{-1}. One of the reasons may be a shift to higher yields of α-radicals at high pH (see above).

The first step in the peroxyl radical decay is their combination to unstable tetroxides which subsequently decay to the stable products [reactions (14)–(16)] (for a review see ref. 37).

$$2\,ROO^{\bullet} \underset{(14/15)}{\rightleftharpoons} ROOOOR \xrightarrow[(16)]{} \text{Products}$$

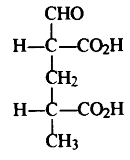


12 **13**

In general, the intermediate tetroxides decay by two types of reactions, the concerted ones [*e.g.* reactions (17) and (18)] and reactions involving oxyl radicals as intermediates [reaction (19)]. Reactions (17) and (18) require α-hydrogens such as are available in the β-peroxyl radicals **9** and **11**. Reaction (19) can be undergone by all types of peroxyl radicals. In addition to these general reactions, the α-peroxyl radicals derived from carboxylic acids can undergo a concerted reaction[26] as depicted in reaction (20) for the α-peroxyl radicals **10** formed in the present system.

Although it is impossible to give a detailed reaction scheme, some consideration as to typical reaction pathways (backed by other studies on peroxyl radical decay; for a review see ref. 37) seems to be appropriate.

In the concerted reactions of the type represented by reaction (17) and in the equivalent disproportionation reactions of the oxyl radicals [*cf.* reaction (19)], the hydroxyl substituted compounds 2-hydroxymethyl-4-methylglutaric acid **16**, 2-hydroxy-2,4-dimethylglutaric acid **17** and 3-hydroxy-2,4-dimethylglutaric acid **18** are formed with a combined *G* value of *G*(**16**–**18**) = 0.4×10^{-7} mol J^{-1}. This value indicates that *ca.* 14% of the peroxyl radicals decay by these routes.



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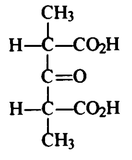

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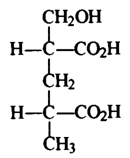

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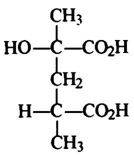

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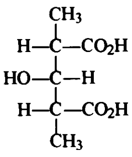
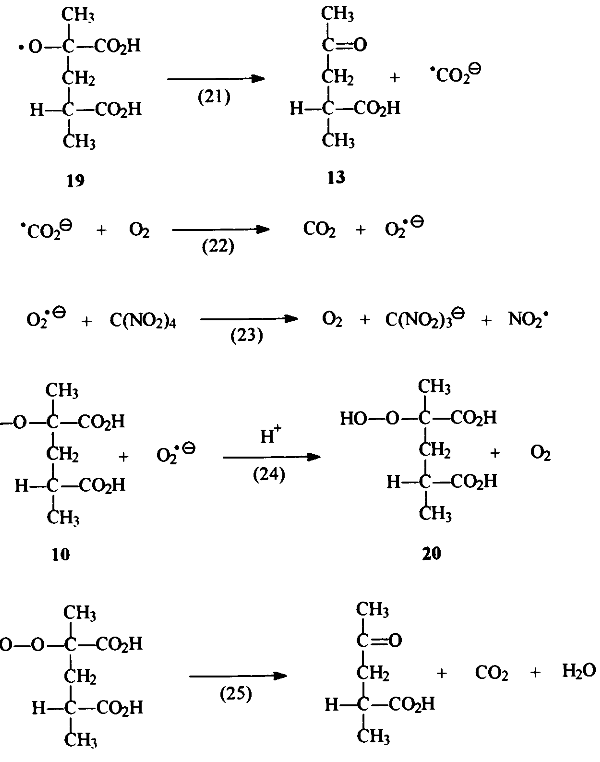


18

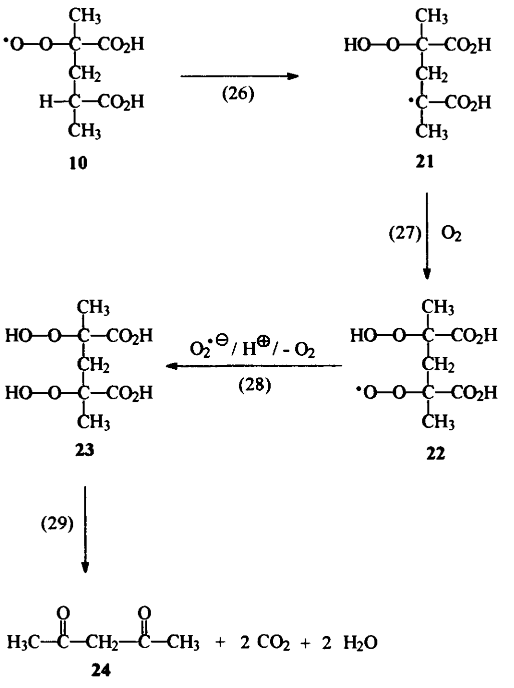
The excess of the carbonyl compounds 2-formyl-4-methylglutaric acid **14** and 2,4-dimethyl-3-oxoglutaric acid **15** [*G*(**14** + **15**) = 1.2×10^{-7} mol J^{-1}] can be taken as evidence that reaction (18) also contributes *ca.* 14%.

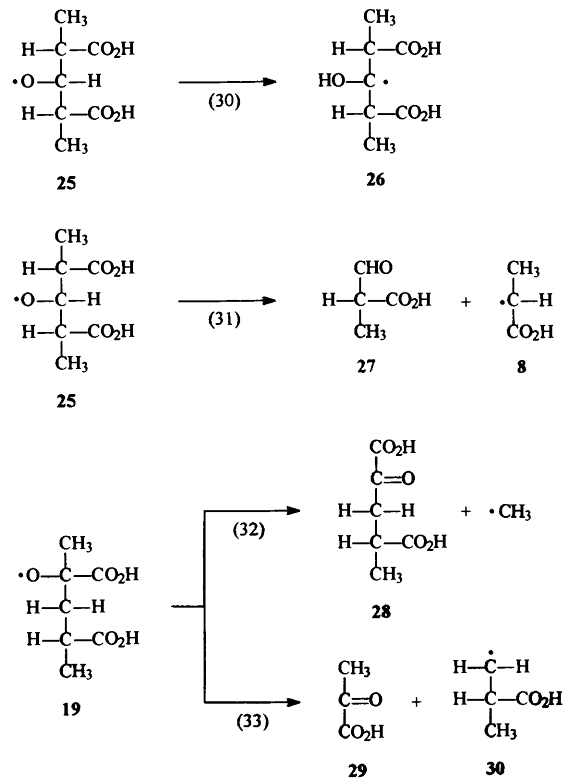
A product formed with a significant yield is 2-methyl-4-oxovaleric acid **13** [*G*(2-methyl-4-oxovaleric acid **13**) = 1.4×10^{-7} mol J^{-1}]. It may be formed in reactions (20), (21) and reaction (24) followed by reaction (25). Reaction (21) [followed by reaction (22) and a disproportionation of the $HO_2^{\bullet}/O_2^{\bullet -}$ radicals] is the free-radical analogue of the concerted reaction (20). Reaction (24) is the well known reduction of peroxyl radicals by $O_2^{\bullet -}$. The decarboxylation reaction (25) is mechanistically analogous to the decarboxylation of β-halogeno-carboxylic acids. The yield of **13** shows that these three routes account for another 25%. The contribution of reactions (21) and (22) can be assessed independently since $O_2^{\bullet -}$ can be determined by the reaction with tetranitromethane [reaction (23)].[38] After corrections for the initial yield of $HO_2^{\bullet}/O_2^{\bullet -}$, *G*(nitroform anions) = $0.8–0.9 \times 10^{-7}$ mol J^{-1} is found for pulse- and γ-radiolytic conditions.



19 **13** **10** **20** **20** **13**

An interesting product is acetylacetone **24** which has two modified sites. Its formation is most likely initiated by an intramolecular H-transfer [reaction (26)] which can proceed *via* a six-membered transition state. Analogous reactions have been observed before with diethyl ether and diisopropyl ether.[39,40] Peroxyl radical **22** can be reduced by $O_2^{\bullet -}$ [reaction (28)] to yield the hydroperoxide **23**. Like **20**, hydroperoxide **23** is unstable and decomposes into acetylacetone **24**, carbon dioxide and water [reaction (29)]. An analogous sequence of reactions has been observed with the PAA-derived peroxyl radicals giving rise to products having spectral properties close to, but not identical to that of acetylacetone.[13] *G*(acetylacetone) = 0.5×10^{-7} mol J^{-1}, *i.e.* 9% of the total radical yield. However, reaction (26) may proceed with a somewhat higher efficiency since there will be other decay routes of **22** not leading to acetylacetone.





A very rough estimate of the rate constant of reaction (26) can be obtained from the lifetime of the peroxyl radicals within which this reaction must occur with relatively high efficiency. Considering only the bimolecular decay of the peroxyl radicals and using its rate constant at pH 3.6, half-lives of *ca.* 0.4 s have been calculated for the given dose rate. Within that lifetime approximately one third of the peroxyl radicals **10** undergo reaction (26). The rate constant of the intramolecular H-abstraction (26) should therefore be of the order of $k_{26} \approx 0.5\ s^{-1}$.

Reactions of $HO_2^{\bullet}/O_2^{\bullet-}$ with peroxyl radicals **9** and **11** lead to hydroperoxides which are probably more stable than **20** and **23** and hence can be detected by the modified Allen's method [G(total organic hydroperoxides) $= 0.3 \times 10^{-7}$ mol J^{-1}].

Oxyl radicals can combine, undergo 1,2-H shifts and fragmentations. On the basis of previous data on acetate[26] we assume that the 1,2-H shift [reaction (30)] of oxyl radical **25** proceeds only to a very limited extent. Studies on the acetate[26] and on the methylperoxyl radicals[41] have shown that a combination of oxyl radicals was of minor importance. This should apply also to the present system. However, scission processes seem to be among the major reactions of the oxyl radicals **25** and **19** [reactions (31), (32) and (33); for competing reactions see reactions (30) and (21)]. Also, peroxyl radical **9** may give rise to oxyl radicals, but the expected fragmentation product formaldehyde was not observed in related systems[42] nor is formaldehyde a major product in the present system (see Table 1).

Scission products were found with a total G value of 1×10^{-7} mol J^{-1}, *i.e.* close to 10% of the peroxyl radicals. These fragmentation products were not analysed in detail. Those identified so far include 2-methylmalonaldehydic acid **27** ($G \approx 0.2 \times 10^{-7}$ mol J^{-1}), acetaldehyde ($G \approx 0.25 \times 10^{-7}$ mol J^{-1}), formaldehyde ($G \approx 0.1 \times 10^{-7}$ mol J^{-1}) as well as small amounts of 2-oxopropionic acid, propionaldehyde and acetone.

Note that scission [reactions (31)–(33)] is not a radical-terminating process. The resulting carbon-centred radicals react with oxygen to yield new peroxyl radicals capable of reacting with the substrate radicals, thus further complicating the already complex reaction scheme.

As concerns the PAA-derived peroxyl radicals, fragmentation reactions are of importance and result in a decrease in the average molecular weight of the polymer.[8] The yield of breaks, however, is expected to remain limited, because the termination reactions should prevail. Indeed, at pH 3 scission occurs with a G value of only 0.9×10^{-7} mol J^{-1}.[43]

Conclusions

In the course of the study of the reactions of the radicals derived from 2,4-dimethylglutaric acid information has been gathered which leads to an understanding of major aspects of the radical reactions of poly(acrylic acid), PAA, *e.g.* the pH dependence of the crosslinking yield in the absence of oxygen and the dominance of disproportionation reactions in this system. In the presence of oxygen, acetylacetone-like products had been observed as major products in the polymer[13,43] and a mechanism as discussed here for the formation of acetylacetone had been suggested (without, however, the benefit of having identified the corresponding product). The identification of acetylacetone in the present study now adds weight to this proposal.

It remains true that the polymer structure and the long lifetimes of the PAA radicals allow reactions to proceed which are not observed with our low molecular weight model system. These additional reactions are mainly the transformation of β-radicals into α-radicals and scission reactions of the α-radicals in the absence of oxygen.[13,14,33]

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