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Radiolytic redistribution of H and O atoms in acetylacetone

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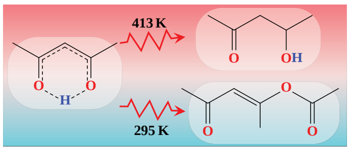
Compared to ambient conditions, radiolysis of boiling acetylacetone almost halved the yield of C–OH bond cleavage and doubled the redistribution of H atoms.



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Acetylacetone (AA) is a unique medium for studying primary ion–molecular reactions induced by radiolysis. Under ambient conditions, its enol form, 4-hydroxypent-3-en-2-one, predominates over the diketo form, pentane-2,4-dione. This is due to strong intramolecular hydrogen bonds and conjugated double bonds, which together provide resonance stabilization of the enol.[1–3] This work is the first study of radiolytic bond cleavage in acetylacetone based on a comparison of radiolysis products at room temperature (295 K) and boiling point (413 K), *i.e*. in the presence and in the absence of hydrogen bonds.[†]

Radiolysis of AA leads to cleavage of both the central C(2)–C(3) bond and side bonds (Figure 1). Most cleavages are due to fragmentation of primary excited radical cations or their reaction with AA molecules [Figure 2, equations (1)–(5)]. Similar fragmentation processes take place in excited molecules. The most significant differences at 295 and 413 K relate to the cleavage of C–OH, O–H, and C–H bonds, *i.e*. most involved in hydrogen bonding and proton transfer.

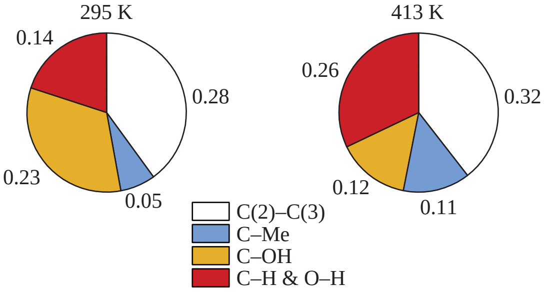

Figure 1 Radiation-chemical yields (μmol J^{-1}) of bond cleavage at 295 and 413 K.

According to the Franck–Condon principle,[4] a molecular radical cation generated by ionization initially has the same structure as an enol molecule stabilized by a conjugation system and an intramolecular hydrogen bond. This should cause structural stress in the radical cation, which, in turn, is fraught with its fragmentation.[5–7] As a consequence, the efficiency of fragmentation depends on the possibility and rate of structural relaxation of the intermediate. Undoubtedly, the boiling state promotes faster relaxation.

Post-ionization reactions form up to 30 compounds; however, six of them are predominant (acetone, acetic acid, CO, 4-oxopent-

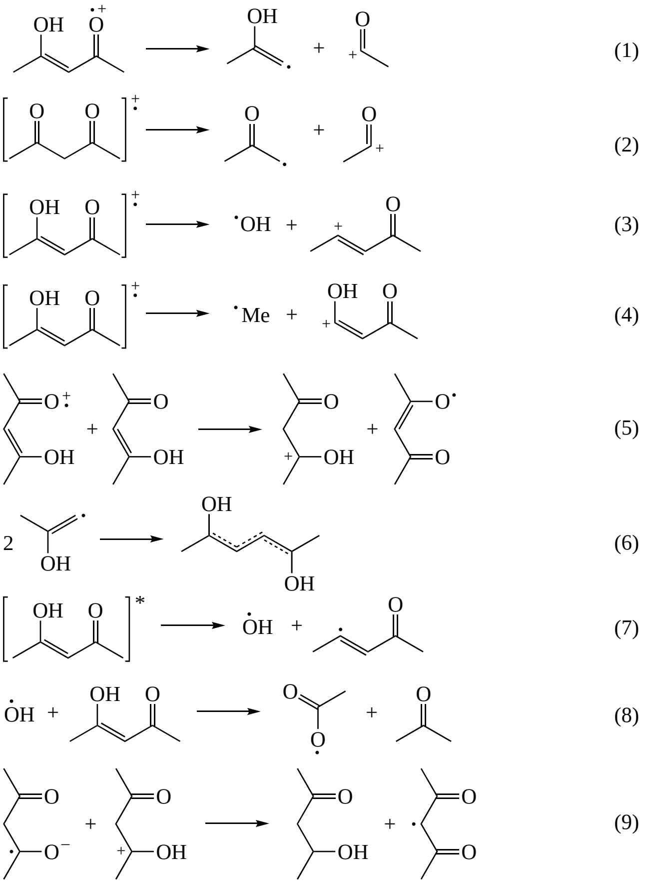

Figure 2 Initial radiolytic reactions in acetylacetone.

[†] Acetylacetone (Carl Roth GmbH) was used after drying and three times airless distillation. The radiation source was a LINS-03-350 linear electron accelerator, generating a 3-MeV electron beam at a dose rate of 2.7 ± 0.1 Gy per pulse (1000 kGy s^{-1} during the pulse). The experiments used 50 pulses per second in a 20–180 kGy range of absorbed dose. A phenazine dye-doped copolymer film Certified Reference Material SO PD(F)R-5/50 was used as a dosimeter. The composition of the samples was analyzed immediately after irradiation using a gas chromatograph with a mass spectrometer (Agilent 5977EMSD/7820AGC, helium, 60-m glass capillary column of 0.25 μm inner diameter, NIST library).

2-en-2-yl acetate, 4-hydroxypentan-2-one, and 1,1,2,2-tetraacetylethane), whose yield *G* is almost 4/5 of the total yield of the products (0.56 and 0.93 μmol J^{-1} at 295 and 413 K, respectively). Accordingly, these six compounds characterize key transformations. Both temperatures provide the highest yield for C(2)–C(3) bond cleavage (see Figure 1). The main resultant products are acetone (*G* 0.10 and 0.16) and acetic acid (*G* 0.16 and 0.11). On the other hand, acetic acid, like 4-oxopent-2-en-2-yl acetate (*G* 0.07 and 0.007), originates from C–OH bond cleavage. Cleavage of the C–Me bond is the source of CO and various radical combination products involving the methyl radical. The main products of hydrogen redistribution are 4-hydroxypentan-2-one (*G* 0 and 0.24) and tautomeric forms of dimeric 1,1,2,2-tetraacetylethane (*G* 0.04 and 0.08).

The radiation energy predominantly affects the enol form, since it is dominant (~80%) and its lower ionization potential (9.08 eV *vs.* 9.63 eV for the diketo form) promotes energy and charge transfer from the diketone to the enol.[8] In particular, the predominant degradation of the enol form is manifested in the formation of hexane-2,5-dione isomers. The product of C(2)–C(3) bond cleavage in the diketone should be 2-oxopropyl [Figure 2, equation (2)]; therefore, the dimerization product of these radicals should be hexane-2,5-dione.[5] However, at 295 K, hexa-2,4-diene-2,5-diol is formed instead of hexane-2,5-dione. In turn, radiolysis at 413 K generates both hexane-2,5-dione and hexa-2,4-diene-2,5-diol. Apparently, cleavage of the C(2)–C(3) bond of the enol [see Figure 2, equation (1)], being dominant, leads to 2-hydroxyprop-1-en-1-yl, the dimerization of which produces hexa-2,4-diene-2,5-diol [equation (6)], where π-electron density is delocalized with the participation of four C atoms. The alternation of double and single C–C bonds is the same as that in buta-1,3-diene, which ensures the stability of the dimer. The p-orbitals involved in the formation of bonds are located not on the line between the nuclei, but in a perpendicular plane, which allows them to overlap in all directions.[9] Thus, the p-orbital of the C(3) atom interacts with the orbitals of both the C(2) and C(4) atoms. Due to conjugation, the mass spectrum of this dimer differs from that of hexane-2,5-dione by a significantly higher relative intensity of masses 99 and 114 (Figure 3). Boiling accelerates the conversion of 2-hydroxyprop-1-en-1-yl to 2-oxopropyl. Thus, the formation of hexane-2,5-dione becomes probable both *via* the dimerization of 2-oxopropyl radicals and *via* the combination of 2-oxopropyl with 2-hydroxyprop-1-en-1-yl. Such a combination does not give a stable conjugation, since the hydroxy group next to the isolated double bond is easily converted into a carbonyl.[9]

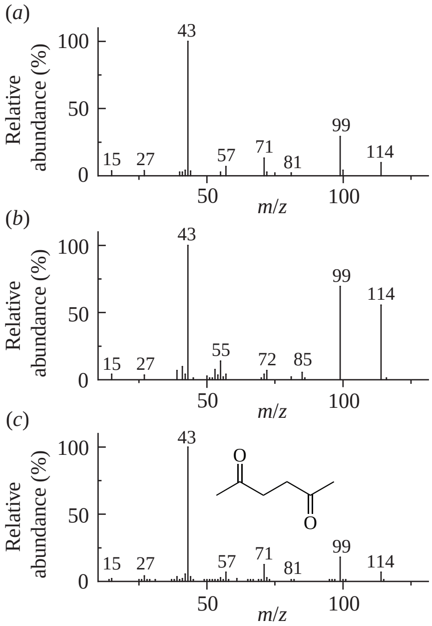

Figure 3 Observed mass spectra of (*a*) hexane-2,5-dione and (*b*) hexa-2,4-diene-2,5-diol compared to (*c*) NIST library mass spectrum.

The C(2)–C(3) bond cleavage yield weakly depends on temperature (see Figure 1), which agrees with the Franck–Condon principle. Accordingly, all observed differences in yields are due to post-ionization processes. A slight increase in the C(2)–C(3) bond cleavage yield at 413 K is associated with a weakening of the ‘cage’ effect (the Franck–Rabinowitch mechanism),[4] *i.e.* with a decrease in AA regeneration. The higher observed yield of C–Me bond cleavage at 413 K is due to increased thermal fragmentation of radicals (first of all, acetyl) with elimination of CO. The most probable is the simultaneous formation of the methyl radical and CO.[4,5,10]

The yield of C–OH bond cleavage at 295 K is almost two times higher than that at 413 K. Moreover, the yield of acetic acid is the highest among light products, and the yield of 4-oxopent-2-en-2-yl acetate is the highest among products that are heavier than AA. High yields indicate the formation of these products in primary nonhomogeneous processes at high concentrations of the participating intermediates. Even at doses of 20–36 kGy, when there is little acetic acid, acetate is formed at 295 K in a high yield, while at 413 K the yield is very low even at 180 kGy, when there is a lot of acid. Obviously, the precursors of 4-oxopent-2-en-2-yl acetate at 295 K are formed almost simultaneously and are close to each other. Such precursors can be the acetyl cation [see Figure 2, equations (1) and (2)], as well as the OH radical, which arises *via* the fragmentation of radical cations and excited AA molecules [equations (3) and (7)].

The elimination of OH is observed even in the gas phase.[1,11] In liquid AA, a high dipole moment and a high concentration of dipoles per unit volume contribute to the orientational (dipole) polarization of bonds. Like in liquid 2-hydroxypropene and aliphatic alcohols,[5–7] polarization facilitates C–OH bond cleavage. In turn, double bonds are effective scavengers of the OH radical,[12–14] leading in the case of AA to acetone and acetoxy radical [see Figure 2, equation (8)]. The sequence of fast reactions [equations (7) and (8)] ensures the proximity of 4-oxopent-3-en-2-yl and acetoxy radicals to each other. At 295 K, they are in a ‘cage’ and inevitably combine, giving 4-oxopent-2-en-2-yl acetate in a high yield. Boiling, weakening structural stresses, reduces the probability of C–OH bond cleavage, and also promotes the release of radicals from the ‘cage’. As a consequence, the yield of 4-oxopent-2-en-2-yl acetate at 413 K becomes much lower.

The formation of 4-hydroxypentan-2-one at 413 K occurs due to proton transfer [see Figure 2, equation (5)] and subsequent neutralization with the participation of the radical anion [equation (9)]. The absence of this alcohol at 295 K indicates the suppression of proton transfer and neutralization reactions [equations (5) and (9)], while the high yield at 413 K indicates the elimination of such obstacles. Most likely, a strong intramolecular hydrogen bond in enol molecules prevents proton transfer.[1–3] Under structural stresses, the fragmentation of the radical cation at 295 K can occur earlier than proton transfer [equation (5)]. Boiling AA becomes less viscous and free from hydrogen bonds while vibrations and rotations of its skeletal bonds are intensified. Accordingly, the boiling mode promotes rapid non-dissociative relaxation of the primary radical cation and, thus, its participation in proton transfer. Proton transfer and neutralization [equations (5) and (9)] proceed mainly with the participation of the hydroxy group leading to the 4-oxopent-2-en-2-yloxy radical. This radical, along with other alkoxy radicals prone to H-abstraction, makes a large contribution to the doubling of the H-redistribution at 413 K compared to 295 K.

In conclusion, thermally driven control of hydrogen bonds makes it possible to significantly change the radiation resistance of acetylacetone, primarily the yield of radiolytic cleavage of C–OH and O–H bonds, thereby providing a significant change in the composition and yield of final radiolysis products.

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