Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2021, **31**, 558–560
Mendeleev Communications

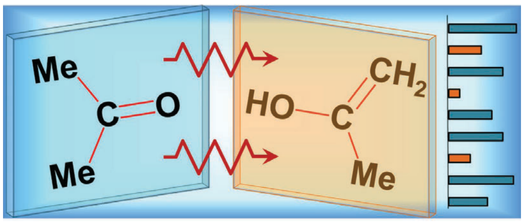
Enolization in the radiolysis of acetone

Diana N. Imatdinova, Sergey I. Vlasov and Alexander V. Ponomarev*

A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russian Federation. Fax: +7 495 335 1778; e-mail: ponomarev@ipc.rssi.ru

DOI: 10.1016/j.mencom.2021.07.041

Radiolytic transformations in acetone proceed with the direct participation of its enol tautomer and its derivatives formed as a result of isomerization of excited molecules and ions, as well as chemical reactions catalyzed by acidic products of radiolysis.



Keywords: radiolysis, acetone, enolization, propen-2-ol, dose rate, temperature effect, chemical condensation.

Knowledge of the excitation, ionization, and isomerization of acetone molecules serves as a starting point in the study of the mechanism of radiolysis and photolysis of carbonyl compounds, in the diagnosis of diseases complicated by diabetes, as well as in monitoring the state of the upper atmosphere.[1–3] Excess energy provokes the dynamic isomerization of the keto form of acetone into the enol form (propen-2-ol). Similar processes are manifested in the MacLafferty rearrangement,[4,5] which plays an important role in mass spectrometry, pyrolysis, and many organic synthesis processes.[6,7] The study of propen-2-ol is difficult due to its rapid ketonization. The keto form is 42.5 kJ mol^{-1} (0.44 eV per molecule) energetically more favorable than the enol. Under ambient conditions, the enol content in acetone does not exceed 0.0001%.

Previously, the role of enolization in the radiolysis of acetone was not taken into account. At the same time, radiolysis generates excited molecules, ions and radicals, whose energy is sufficient for enolization, and intermediates with acidic or basic properties are able to further catalyze it. Accordingly, the enol form can significantly participate in the intermediate stages of radiolysis. In this work, enolization is considered based on a comparison of the radiolysis products of acetone at different temperatures and a high dose rate of an electron beam.[†]

The change in the composition of the radiolysis products depending on the acetone temperature is shown in Figure 1. Initial yields are given, determined from dose dependences of yields by extrapolation to zero dose. Among the products, 2-acetoxypropene, 2-methoxypropene, vinyl acetate, and some other compounds were found that can be classified as products of a combination with the participation of enol-type radicals, 2-propenoxy (ER1) and vinyloxy (ER2). These radicals can be considered as isomers of two other known radicals, 2-oxopropyl (KR1) and acetyl (KR2), respectively. However, direct isomerization of KR1 to ER1 and KR2 to ER2 at 329.5 K is insignificant.[8,9] Consequently, ER1 and ER2 can be formed predominantly from excited molecules or radical cations.

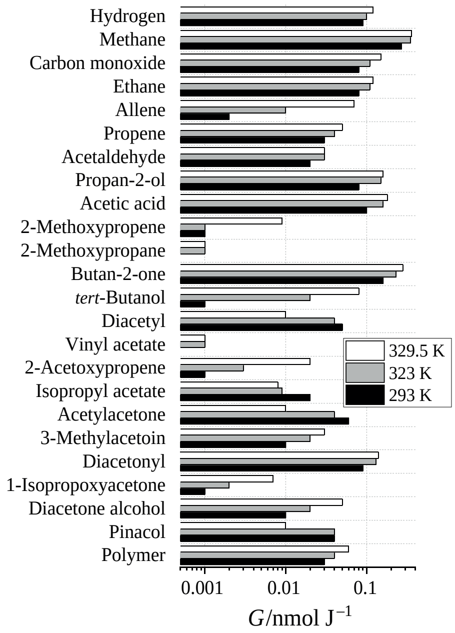


Figure 1 Initial radiation-chemical yields *G* of the main products of the acetone radiolysis depending on temperature.

[†] Acetone (99%, REACHIM) was dried over anhydrous $CaSO_4$ and silica gel and then distilled three times in an Ar atmosphere. Irradiation was carried out with 3 MeV electrons (LINS-03-350 linear accelerator; average beam current, ⩽ 350 μA) in an electrically heated quartz cell in an Ar atmosphere. The maximum dose rate during the pulse was 1000 kGy s^{-1}. To avoid overheating of the sample, an intermittent irradiation mode with an average dose rate of 5 kGy min^{-1} (20 pulses per second) was used. Phenazine dye-doped copolymer film standard reference material SO PD(F)R-5/50 [GSO (Certified Reference Material) no. 7875–2000] was used as dosimeter. No later than 5 min after the completion of irradiation, the samples were fed to a gas chromatograph with a mass spectrometer (Agilent 5977EMSD/7820AGC, helium, glass capillary column 60 m long with an internal diameter of 0.25 μm, NIST library).

Such alkoxy radicals are capable of rapid H abstraction (with the formation of propen-2-ol and ethenol, respectively) or of addition to a double bond with the formation of heavier alkoxy radicals, precursors of high-molecular-weight products.[10–12] Accordingly, due to the high concentration of acetone molecules, ER1 and ER2 quickly decay in reactions with a solvent and, as a consequence, take limited participation in radical recombination. Therefore, enol products were not previously detected during γ-radiolysis (at ⩽ 10 Gy s^{-1}), but they are noticeable at a high dose rate provided by powerful electron pulses.

The catalytic pathway for the conversion of acetone to propen-2-ol consists in the abstraction of a proton with the formation of an enolate anion, or in the protonation of the carbonyl group (Figure 2). Radiolysis leads to the formation of the same enolate anion as a result of the dissociative addition of an excitation electron to the keto form [Figure 3, equation (1)]. In turn, the same cation is generated in the reaction of the primary radical cation with the keto form [equation (2)]. Subsequent neutralization of the ions results in the formation of two molecules, at least one of which is enol [equation (3)]. A similar result follows from neutralization with the participation of excited radical cations and radical anions [equations (4) and (5)]. In parallel, the presence of enol promotes the formation of 2-hydroxypropyl radicals [equation (6)]. The combination of these radicals with methyl produces *tert*-butanol, which was not previously detected in γ-radiolysis, but is one of the main products of electron beam radiolysis, especially in boiling acetone.

The radiation resistance of enol form differs significantly from that of the ketone. The ionization potential (8.6 eV) of the enol is lower than that of the ketone (9.7 eV), while the molecular cation radical of enol is more stable than that of acetone.[6] In the gas phase, the threshold fragmentation energy of radical cations $CH_2{=}C(Me){-}OH^{\bullet+}$ and $(Me)_2C{=}O^{\bullet+}$ to $MeCO^+$ and $^{\bullet}Me$ is 11.03 and 10.45 eV, respectively. The threshold energy for the decay of the enol radical cation into $CH_2{=}C{=}OH^+$ and $^{\bullet}Me$ is about 12.2 eV.[6] Moreover, the acetone radical cation can decay with the elimination of both $^{\bullet}Me$ and CH_4 (in a narrow energy range). In the case of enol radical cations, CH_4 elimination is not observed or is not noticeable against the background of the predominant fragmentation of keto form radical cations.[5]

As a result of ionization, the primary radical cation center is located mainly on the oxygen atom; however, due to excitation, various instantaneous configurations of the radical cation are possible. The rate constants for the disappearance of the radical cation and the radical anion of acetone are $\sim 1\times 10^7$ s^{-1} and 6.4×10^5 s^{-1}, respectively.[13] Consequently, these ions have enough time and excess energy (4 ± 2 eV) for isomerization and participation in reaction [see Figure 3, equation (2)] before neutralization. In the course of ion-molecular clustering,[14] meeting with enol form most likely leads to the addition of a carbocation at the C=C bond of the enol with the formation of a new C–C bond. However, the excess energy of the resulting combined intermediate promotes bond cleavage in the β-position relative to the unpaired electron [equation (7)]. Subsequent neutralization of the new cation forms butan-2-one. This process may be one of the reasons for the dominance of butan-2-one among the heavy radiolysis products of boiling acetone (see Figure 1).

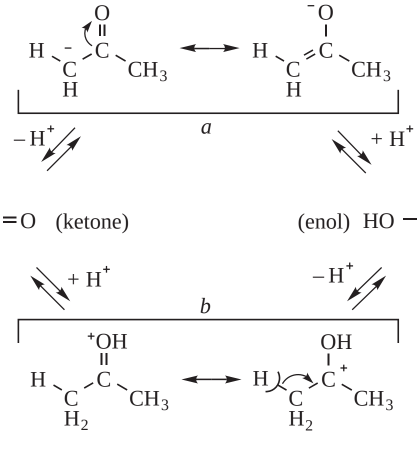


Figure 2 Enolization of acetone *via* (*a*) basic and (*b*) acidic catalysis.

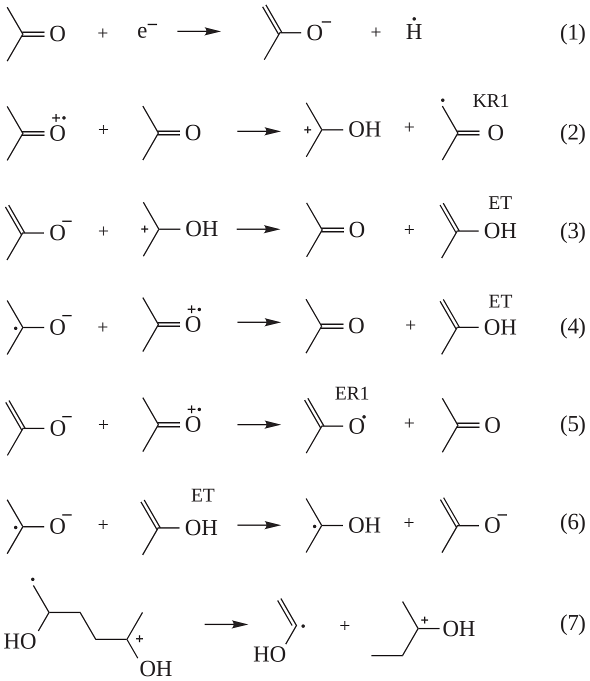


Figure 3 Reactions involving enol intermediates.

Allene and water formation is important evidence for enol involvement in radiolysis. Unlike acetone, excited enol possessing a hydroxy group and a mobile α-H atom can undergo cleavage of the C–O bond. In C_1–C_4 alcohols, the yield of C–O bond cleavage is 0.04–0.08 μmol J^{-1}, and the highest yield is observed for isopropyl alcohol. In boiling propan-1-ol, the yield of water reaches 0.1 μmol J^{-1}.[15] In this work, the radiolysis of boiling acetone also leads to the formation of water, and the allene yield is 0.07 μmol J^{-1}. The $^{\bullet}OH$ radical is a precursor not only of water, but also of acetic acid (in combination with KR2 or ER2). However, due to the short lifetime of $^{\bullet}OH$, the well-known reaction of water with ketene is a more competitive route for the formation of acetic acid.[15] Dehydration of aldols and ketols generated by chemical condensation (aldol-crotonic condensation) with the participation of the very enol and enol intermediates can also serve as a source of water. In this case, the unsaturated products serve as scavengers for radiation-induced radicals, thereby contributing to the irregular structure of the resulting polymers.

An increase in the H_2 yield with raising the temperature can also be associated with enolization. The dissociation of the C–H bond in ions and in excited acetone molecules occurs at energy 3–4 eV higher than the dissociation of the C–C bond.[3] The excitation yield during radiolysis is practically independent of temperature, and the role of decomposition of acetone radicals in the temperature range of 293–329 K is insignificant. Nevertheless, the observed H_2 yield increases with heating by more than 1.3 times. Cleavage of the O–H bond in enol, as in alcohol, can serve as an alternative source of H_2. For example, the yield of alkoxy radicals in C_1–C_3 alcohols is 0.10–0.26 μmol J^{-1}.[15] In enols, as in alcohols, there is a high probability of dissociative addition of an electron, as well as the decay of a radical cation or an excited molecule with the elimination of an H atom from the hydroxy group. The subsequent transformation of H into H_2 is provided by H-abstraction reactions with the participation of surrounding molecules.

Thus, ionization and excitation promote the dynamic isomerization of acetone to propen-2-ol. In place of the carbonyl group (the C=O bond energy is about 7.8 eV), the C–O and O–H bonds are formed (energies of about 3.7 and 4.4 eV, respectively), whose cleavage of causes a change in the composition of radiolysis products with an increase in the temperature and dose rate of ionizing radiation. Irradiation of boiling acetone increases the yields of hydrogen, water, alcohols and products of the enol structure, as well as high molecular weight compounds. Primary radicals resulting from the cleavage of the O–H bond (vinyloxy and 2-propenoxy) are short-lived alkoxy radicals that are highly reactive in H abstraction and addition to double bonds. This prevents their direct observation, but manifests itself in the formation of specific end products. Carbonyl products are involved in the radiolytic transformations of many organic compounds, especially under aerobic conditions. Therefore, it is important to take into account the radiation-stimulated enolization of carbonyl intermediates, since it can significantly affect the radiolysis mechanism and expand the range of final products.

References

1 A. L. F. de Barros, D. P. P. Andrade, E. F. da Silveira, K. F. Alcantara, P. Boduch and H. Rothard, *Mon. Not. R. Astron. Soc*., 2018, **474**, 1469.
2 M. Shokrekhodaei and S. Quinones, *Sensors (Basel)*, 2020, **20**, 1251.
3 M. Nobre, A. Fernandes, F. Ferreira da Silva, R. Antunes, D. Almeida, V. Kokhan, S. V. Hoffmann, N. J. Mason, S. Eden and P. Limão-Vieira, *Phys. Chem. Chem. Phys.*, 2008, **10**, 550.
4 D. J. McAdoo, *Mass Spectrom. Rev*., 2000, **19**, 38.
5 G. Bouchoux, *Mass Spectrom. Rev*., 1988, **7**, 1.
6 E. Grajales-González, M. Monge-Palacios and S. M. Sarathy, *J. Phys. Chem. A*, 2018, **122**, 3547.
7 A. V. Ponomarev and B. G. Ershov, *Mendeleev Commun*., 2019, **29**, 589.
8 H. Wakamatsu and Y. Hidaka, *Int. J. Chem. Kinet*., 2008, **40**, 320.
9 H. Wang and J. W. Bozzelli, *ChemPhysChem*, 2016, **17**, 1983.
10 A. V. Ponomarev and E. M. Kholodkova, *Mendeleev Commun*., 2018, **28**, 375.
11 T. P. Zhestkova, T. N. Zhukova, A. V. Ponomarev and I. G. Tananaev, *Mendeleev Commun*., 2008, **18**, 338.
12 T. S. Dibble and J. Chai, in *Advances in Atmospheric Chemistry*, eds. J. R. Barker, A. L. Steiner and T. J. Wallington, World Scientific, New Jersey, 2017, vol. 1, ch. 3, pp. 185–269.
13 A. V. Ponomarev, A. M. Ratner and A. K. Pikaev, *High Energy Chem.*, 1995, **29**, 91 (*Khim. Vys. Energ.*, 1995, **29**, 101).
14 V. Feldman, F. Sukhov, A. Orlov and I. Tyulpina, *Phys. Chem. Chem. Phys*., 2003, **5**, 1769.
15 A. V. Ponomarev, S. I. Vlasov, E. M. Kholodkova, V. N. Chulkov and A. V. Bludenko, *Radiat. Phys. Chem.*, 2019, **165**, 108405.

Received: 2nd March 2021; Com. 21/6472