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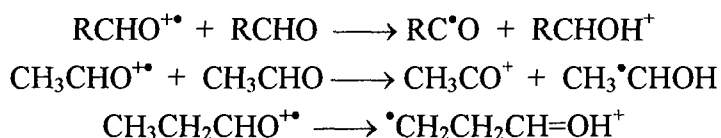
RADICAL CATIONS IN RADIATION CHEMISTRY OF ALDEHYDES: ESR STUDY AND QUANTUM CHEMICAL ANALYSIS

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Quantum-chemical (MNDU-UHF) calculations of electronic, spin and energy characteristics of radical cations (RC) of ethanal, propanal, butanal, and pentanal and their distonic isomers were performed. The calculations both with "frozen" (vertical ionization) and completely optimized geometry (adiabatic approximation) were made. It was shown that the most positive charge and spin population are localized at O atoms and adjacent C atom as well as at aldehyde protons. The C-H bonds corresponding to those protons as well as neighboring C-O and C-C bonds are considerably weaker (longer) in radical cations as compared to their neutral precursors. That is why such reaction centers are apt to deprotonation with the formation of acyl radical as well as to α - and β -splitting (scission) which are well-known from aldehydes mass-spectra. Our calculations show that distonic RC (products of intramolecular H-atom transfer) are more stable as compared to their classical isomers: e.g. the difference in energy $\Delta E = -0.95$ eV, -1.2 eV, and -1.5 eV for three distonic isomers of butanal RC as compared to classical isomer, $\Delta E = -1.2$ eV for distonic RC of ethanal. The results of calculations are effectively correlated with ESR data obtained in freonic solutions, X- and gamma-irradiated at 77 K and in liquid aldehydes, X-irradiated by using 2,4,6-tri-tert-butyl nitrosobenzene (BNB) and t-BuNO (NtB) as spin traps.

RC[•]O radicals as a product of deprotonation of RC, as well as CH₃[•]CHOH radical as a product of H-atom transfer, and also the radicals CH₃CHCH=OH⁺, [•]CH₂CH₂CH=OH⁺ in propanal and [•]CH₂CH₂CH₂CH=OH⁺ in butanal (products of rearrangement of classical RC into their distonic forms) are recorded in ESR spectra in freonic matrices and in liquid aldehydes (spin trapping data: e.g. adduct BNB with [•]CH₂CH₂CH₂CH=OH⁺ in butanal multiplet $3 \times 3 \times 3$ $a^N = 13.5$ G, $a(2H-\beta) = 18.1$ G, $a(2H-m) = 0.8$ G)



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