Mechanisms of the excited-state generation by nicotine-containing aerosols and their prooxidant and antioxidant activities

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Abstract

Tobacco smoke and emissions from electronic nicotine delivery systems (ENDS) constitute chemically complex aerosols, whose biological impact involves triggering the oxidative stress, a well-known risk factor of numerous pathogenic developments in a human organism. In this context, prooxidant and antioxidant activities of such aerosols are of prime interest. These chemically and biologically active media generate a whole set of reactive oxygen species (ROS). Distinguishing experimentally between individual ROS in such complex environments furnishes a formidable task. Thus, it is customary to look for the total measure of them and to monitor their overall effects. Since ROS are prone to generating the electronically excited products in their reactions manifested by the light emission, the chemiluminescence methodology should provide an efficient tool to monitor these aggressive reactants. Tobacco smoke generates directly a rather intensive chemiluminescence [1], whose mechanism involves chemiexcitation in a unimolecular transformation of the smoke-borne free-radical species. However, the concentration of these radicals, [r], obeys a bimolecular (second-order) kinetics and depends on a particulate-phase content (total particulate matter, TPM) of the smoke. The decrease of [r] with increasing the TPM amount manifests antioxidant (radical-scavenging) propensity of the smoke particulate phase. Conversely, aerosols derived from ENDS exhibit no direct chemiluminescence, and for assaying the ROS generation in ENDS emissions we had to use luminol as the pertinent chemiluminescent reactant. We have established for the first time that the formation of harmful oxidation products in the ENDS aerosols proceeds through the free-radical chain mechanism and intervention of hydroperoxides of propylene glycol (solvent for nicotine in ENDS), which are potential prooxidants (ROS sources) able to cause oxidative damage of biomolecules. Contrary to the smoke constituents, aerosols derived from ENDS reveal no significant antioxidant activity.

1. G.F. Fedorova, V.A. Menshov, A.V. Trofimov, Yu.B. Tsaplev, R.F. Vasil'ev, O.I. Yablonskaya, *Photochem. Photobiol.* **2017**, *93*, 579-589.

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