Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 654–656

Direct UVC photodegradation of imipramine in aqueous solutions: a mechanistic study

Ekaterina D. Mordvinova, Olga A. Snytnikova, Victoria A. Salomatova, Vadim V. Yanshole, Vyacheslav P. Grivin and Ivan P. Pozdnyakov

Imipramine hydrochloride (IMI, ≥99%, Sigma) and desipramine hydrochloride (DMI, ≥98%, Sigma), were used as purchased. pH value was controlled by ion-meter ANION-4100 (LTD Infraspak-Analit, Russia) with combined electrode ESK-10614. Analytical grade NaOH or $HClO_4$ were used for pH adjustment. Deionized water was used for the preparation of solutions. Stationary photolysis experiments were carried out in quartz cells with an optical path of 5 cm and a total volume of 10 ml at the temperature of 298 K. Flash photolysis experiments were carried out in quartz cells with an optical path of 1 cm and a total volume of 2 ml at the temperature of 298 K. The cells were constantly purged by a flow of high purity argon when carrying out experiments in oxygen-free solutions.

UV-spectra were recorded using Agilent 8453 spectrophotometer (Agilent Technologies). Transient absorption (TA) experiments were carried out by laser flash photolysis, using the third harmonic (355 nm) of a LS-2137U Nd:YAG laser (Solar, Belarus) as the excitation source (pulse duration, 6 ns; pulse energy, 1-10 mJ; time resolution, ca. 50 ns) as described [I. P. Pozdnyakov, V. F. Plyusnin, V. P. Grivin, D. Y. Vorobyev, N. M. Bazhin and E. Vauthey, *J. Photochem. Photobiol. A: Chem.*, 2006, **181,** 37]. A 9 W UVC ozone-free Radium Puritec lamp (OSRAM GmbH, Germany) emitting at 254 nm was used as steady-state irradiation source. To calculate the IMI photoionization and photolysis quantum yields the lamp and laser intensities were determined using a ferrioxalate actinometer in the same photochemical cell [C. Weller, S. Horn and H. Herrmann, *J. Photochem. Photobiol. A: Chem.*, 2013, **255**, 41]. All quantum yields values were evaluated as the average of two independent measurements.

The photodegradation yield of IMI was measured using a LC 1200 high performance liquid chromatography (HPLC) system (Agilent Technologies, USA), equipped with a diode array detector. Separations were performed using a Agilent Zorbax Eclipse RapidResolution XBD-C18 column (4.6 × 100 mm, 80 Å, 1.8 μm). The flow rate was 0.5 ml min^{-1}, using a mixture of mobile phases A (water) and B (acetonitrile), both with the presence of formic acid 0.1% (v/v), with the gradient elution as follows: 0% B (0-3 min), 0-80% B (3-30 min), 80-100% B (30-31 min), 100% B (31-37 min), 100-0% B (37-38 min), 0% B (38-40 min).The injection volume was 80 μl. The chromatograms were

monitored at 230, 250, 280, 335 and 435 nm and the analysis of the obtained results was performed using Agilent ChemStation software.

The photodegradation products were analyzed at the Center of Collective Use «Mass spectrometric investigations» SB RAS on HPLC coupled with electrospray ionization mass spectrometry (HPLC-ESI-MS) system using an UltiMate 3000RS chromatograph (Dionex, Germany) connected to a maXis 4G high-resolution ESI time-of-flight mass spectrometer (Bruker Daltonics, Germany) after the DAD cell. HPLC separations were made using the same column, flow rate, gradient of the same mobile phases and the same injection volume of 80 µl. Mass spectra were acquired in positive ion mode over the 30-1000 m/z range with 1 Hz scan rate. Each HPLC-MS chromatogram contained a calibration segment where sodium formate clusters used as a calibrant were supplied by the syringe pump connected to a ESI source *via* the divert valve. The typical resolution was ca. 50 000 and accuracy <1 ppm. The data obtained were analyzed using DataAnalysis 4.0 software (Bruker Daltonics, Germany). Chemical formulae were reconstructed from the coincidence of theoretical and measured exact masses and isotopic distributions.

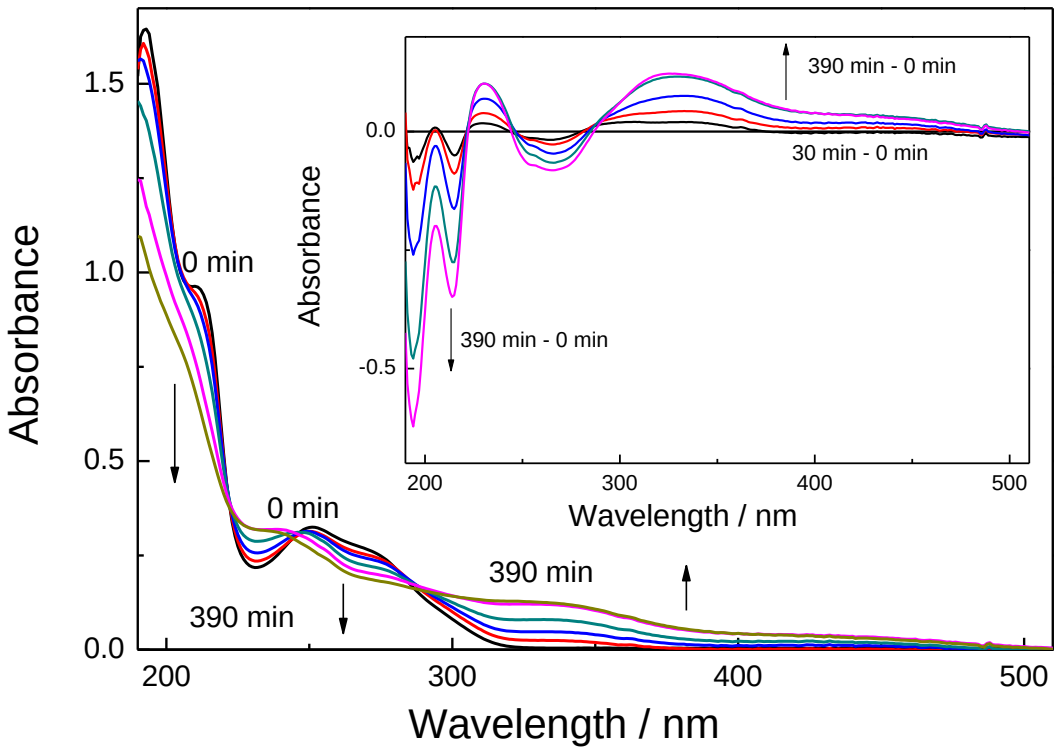

Figure S1 Steady state (254 nm, 0.15 J min^{-1}) photolysis of air-equilibrated IMI (8×10^{-6} mol dm^{-3}) solutions. Evolution of absorption spectra at different irradiation times. Insert – evolution of differential absorption spectra (difference of absorption spectrum at certain time of irradiation and initial spectrum of IMI solution).