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New Photochemical Transformations of 1-Iodopropan-2-one

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Abstract—Photolysis of 1-iodopropan-2-one (λ = 254 nm) at 80–90°C in the absence of CCl_4 was studied. The structure of obtained polymer was studied by ^1H NMR, IR, and ESR spectroscopy.

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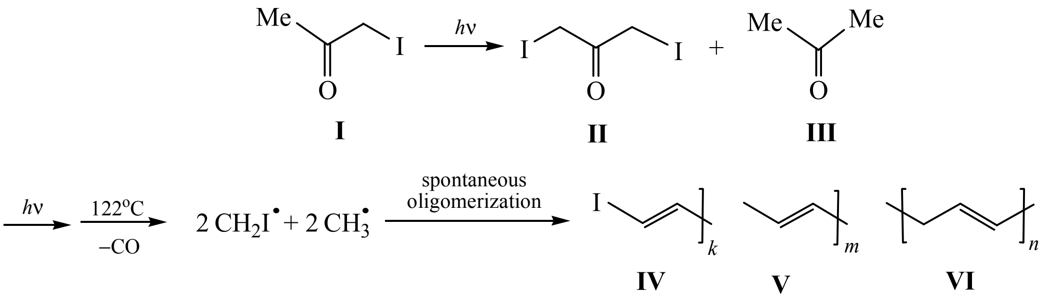
We have studied earlier photochemical transformations of 1-iodopropan-2-one in carbon tetrachloride at λ = 254 nm. It was found that CCl_4 participates in the photolysis so that apart from the products of disproportionation of 1-iodopropan-2-one (1,3-diiodopropan-2-one and acetone) chloroketones were formed [1, 2].

In a hope that the variation of conditions can give this reaction preparative value we have studied the photolysis of 1-iodopropan-2-one (**I**) in an argon atmosphere at 80–90°C and λ = 254 nm in the absence of CCl_4. The reaction was monitored by ^1H and ^{13}C NMR spectroscopy. The obtained spectral data suggest that in the first stage acetone **III** [^1H NMR, δ, ppm: 2.0 (CH_3); ^{13}C NMR, δ, ppm: 29.62 (CH_3), 202.40 (CO)] and 1,3-diiodopropan-2-one (**II**) [^1H NMR, δ, ppm: 3.9 (CH_2I); ^{13}C NMR, δ, ppm: 1.68 (CH_2I); 195.63 (CO)] are formed, as was earlier shown [1]. After 5–6 h the temperature of the reaction mixture rises to 122°C. With this, apparently, carbon monooxide is evolved [3], while the secondary reactions of the formed radicals lead to the formation of black polymers, which were further separated to the soluble (A) and insoluble (B) fractions.

Fraction A was isolated from the total mass of the polymer by treatment with acetone. Polymer A was precipitated from the acetone solution with hexane as a glittering black powder decomposed at 187–190°C. Its molecular mass (M_w) was 4100 with the degree of polydispersity (M_w/M_n) 3.72. From the elemental analysis data, polymer A ccorresponds to $C_{144}H_{304}I_{16}$. The mechanism of the reaction is under investigation. The following tentative scheme of the photolysis can be proposed.



In the ^1H NMR spectrum of fraction A two multiplets are observed at 1.59–1.92 and 5.61–7.77 ppm, which can be assigned to the signals of the CH_3 and =CHI, =CH fragments, respectively. In the ^{13}C NMR spectra of fraction A the methyl carbon signals are observed at 19.22–22.95 ppm and the signals of the

=CHI fragment, at 76.78 ppm. The chemical shifts of the HC= and =C< fragments are registered at 123.76–137.70 and 148.64–154.24 ppm, respectively.

In the IR spectra of the soluble fraction A the absorption bands at 1563 and 1636 cm^{-1} correspond to the C=C bond stretching vibrations in polyconjugated compounds. An intense band at 458 cm^{-1} suggests the presence of an unsaturated =C–I bond. The absorption bands at 2962, 2922, 2852 and 3124 cm^{-1} are characteristic of the C–H vibrations in the CH_3 and CH=C fragments [4]. All this corresponds to the presence of structural fragments **IV–VI** in fraction A.

Investigation of electroconductivity of fractions A and B close in composition has shown that they are high-ohmic organic semiconductors having electroconductivity of 10^{-9} Sm/cm. Solutions of fraction A in chloroform, acetone, acetonitrile form films with high adhesion to various substrates (quartz, glass, aluminum, etc.).

Both fractions, as could be suggested from their deep, almost black color, are paramagnetic and show in the continuous wave ESR spectra similar intense (concentration of paramagnetic centers ca. 10^{19} spin/g) narrow singlet signals with the following parameters (fraction A**:** $g = 2.0056$, $\Delta H = 10.6$ gauss, A/B = 0.84; fraction B**:** $g = 2.0054$, $\Delta H = 9.1$ gauss, A/B = 0.86), corresponding to polymers with extended conjugation system, which is also in agreement with the presence of groups **IV–VI** in the polymer. The signals of both fractions are equally asymmetric (asymmetry parameter A/B < 1), the upper part of the signal (more wide) being described by the Lorentz line and the lower part (more narrow), by the Gauss line, which is indicative of anisotropy of the *g*-factor. Substantial deviation of the *g*-factor from the free electron value is due to interaction of the free electron with heavy iodine atom.

Using the two-pulse ($\pi/2–\tau–\pi$) and three-pulse ($\pi/2–\tau–\pi/2–T–\pi/2$) echo modulation technique at room temperature we have obtained the echo-detected ESR signals. In the former case, for fraction B, the exponential decay of the echo amplitude in semi-logarithmic coordinates gives linear dependence on τ ($R^2 = 0.999$; $n = 14$), that allowed to determine the transverse (spin-spin) relaxation time T_2 equal to 556 ns with high precision. For fraction A the similar dependence was obtained with correlation coefficient 0.990 and the calculated value of T_2 is 625 ns.

The spectral diffusion was assumed to give no contribution to the value of the longitudinal (spin-lattice) relaxation since the concentration of paramagnetic centers in the samples studied was less than 10^{20} spin/g. Rough estimation using the three-pulse echo modulation technique has shown that the dependence of the decay of the echo amplitude on the T value includes contributions from some other relaxation mechanisms and the $T_1–T_2$ model does not allow to reliably estimate time T_1. This suggests, in particular, the absence of ordering in the oligomer structure and requires the use of more complex techniques.

Photochemical polycondensation of 1-iodo-2-propan-2-one. 4 g of 1-iodopropan-2-one (**I**) was irradiated with UV light ($\lambda = 254$ nm) in an argon atmosphere while stirring at 80–90°C for 6–7 h until the temperature raised to 122°C and the reaction mixture became viscous (the reaction was monitored by NMR and TLC). From the obtained viscous mass (20 ml) the soluble part was extracted with acetone. Addition of 60 ml of hexane to the acetone solution resulted in formation of a precipitate which was thoroughly washed with ether to constant weight and dried in a vacuum. Yield 0.3 g (71%), black powder, $T_{\text{decomp.}}$ = 187–190°C. Found, %: C 41.03; H 3.84; I 49.36. $C_{144}H_{304}I_{16}$. Calculated, %: C 42.51; H 7.48; I 50.00. Insoluble in acetone fraction was thoroughly washed with methanol, chloroform, ether to constant weight. Yield 0.6 g, glittering black powder, $T_{\text{decomp.}} >$ 360°C. Found, %: C 42.31; H 3.28; I 47.73.

IR spectra of solid samples were recorded on a Spectrum HE-3100 Varian spectrometer with the attenuated total reflection unit (ATR) on a SeZn glass, and on a FT-IR Vertex 70 Ram II spectrometer. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were registered on a Bruker DPX 400 instrument in $CDCl_3$.

ESR spectra of solid samples were taken on a Bruker ELEXSYS E580 spectrometer at room temperature in continuous-wave and pulse regimes (for primary echo $\pi/2 = 32$ ns, for the echo modulation $\pi/2 = 16$ ns). Relaxation times were estimated from the $T_1–T_2$ model [5]. The molecular mass was determined on a Waters gel chromatograph with flow refractometer detector at 25°C, eluent THF. Specific electric conductivity measurements were performed using a VK2-16 electrometric amplifier. Photolysis of 1-iodopropan-2-one was performed in a quartz flask by irradiation with mercury lamp DRT-230 ($\lambda = 254$ nm). The purity of the isolated products was monitored by TLC on Silufol UV-254 plates with chloroform as eluent.

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