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Kinetics of Heat-Induced and Photochemical Transformations of Quinonimines and Their Derivatives

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Abstract—Heat-induced transformations of N-[2,6-diisopropylphenyl]-3,5-di(*tert*-butyl)-, N-[2,6-diethylphenyl]-3,5-di(*tert*-butyl)-, and N-[2-methyl-6-ethylphenyl]-3,5-di(*tert*-butyl)-o-benzoquinonimines in nonane follow the first-order rate equation, whereas that of N-[2,5-di(*tert*-butyl)phenyl]-3,5-di(*tert*-butyl-o-benzoquinonimine obey the second-order rate equation. Kinetic parameters of these reactions have been determined. 4aH-Phenoxazine derivatives of quinonimines are intermediates of the heat-induced transformations following the first-order kinetics; under the irradiation with 405 nm light they undergo the ring opening to give the starting compounds with quantum yield close to unity.

Keywords: quinonimine, reaction rate order, activation energy, photolysis, 4aH-phenoxazine, reaction rate

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N-Aryl-*o*-benzoquinonimines (**A**) suffer the Diels– Alder reaction in hexane or methanol at room temperature to give dimers (**C**). Initially, the quinonimine undergoes the cyclization into the 4aHphenoxazine (**B**); the reaction is possible only in the case of Z-isomer of the starting compound [1, 2] (Scheme 1).

In this work, we studied reactivity and mechanism of heat-induced and photochemical transformations of





 $c \times 10^{-4}$, mol/L

N-aryl-*o*-benzoquinonimines **I**–**IV** as well as of the products of their thermal decomposition in hydrocarbon medium (Scheme 2).

Heating of compounds **I–IV** in nonane at 283– 373 K induced certain changes in their electron absorption spectra, and the initially red-violet solutions turn yellow-green (Fig. 1).

Heat-induced transformation of quinonimines **I–III** followed the first-order rate equation at conversion up to 70–80% (Fig. 2). The reaction order with respect to the quinonimines was also 1.

Therefore, in the cases of compounds I–III, the rate-limiting stage was the formation of 4aH-phenoxazine derivatives (Scheme 1). Kinetic curves of the consumption of the starting compounds and those of accumulation of final products confirmed the suggested reaction scheme (Fig. 3).

After keeping the solutions with $c = 1 \times 10^{-2}$ mol/L during 2 h at 323 K [mixture (a)] or during 4 h at 373 K [mixture (b)], the solvent was removed from the reaction mixtures under a reduced pressure. In the IR spectra of solids isolated from mixture (a) and (b) the



Fig. 1. Changes of electron absorption spectra of compound I in nonane ($c_0 = 1.8 \times 10^{-3}$ mol/L, 323 K, l = 0.8 cm), thermal transformation during 2000 min.



Fig. 2. Kinetics of heat-induced transformation of compound I in nonane (a) and the same kinetic curve in the coordinates of the first-order reaction (b) ($c_0 = 1.8 \times 10^{-3} \text{ mol/L}$, 313 K).



Fig. 3. Kinetics of transformation of compound **I** in nonane $(c_0 = 2.05 \times 10^{-3} \text{ mol/L}, 343 \text{ K})$. (1) is consumption of **I**, (2) is accumulation of intermediate **B**, (3) is accumulation of dimer **C**.

band assigned to carbonyl group of starting quinones (1555 cm^{-1}) disappeared. In mass spectra of mixture (a) molecular ions and their fragments were observed assigned to the 4a*H*-phenoxazine derivative. Mass spectra of mixture (b) contained the molecular ions of dimer as well.

Heat-induced transformation of compound IV followed the second-order rate equation. As discussed in [2], the Diels–Alder dimerization of 4a*H*-phenoxazine derivative of compound IV is impeded as both the conjugated double bonds in the positions 1 and 3 of IV are shielded by the bulky *tert*-butyl substituents. In the absence of oxygen, the oxazine (B) formed from compound IV could be oxidized with the initial

 Table 1. Rate constant (313 K) and activation energy of heat-induced reactions of quinonimines I–IV

Comp. no.	Rate constant	Activation energy, kJ/mol		
Ι	$k_{\rm I} = 4.1 \times 10^{-4} {\rm s}^{-1}$	75±4		
II	$k_{\rm I} = 3.6 \times 10^{-4} {\rm s}^{-1}$	76±4		
III	$k_{\rm I} = 3.4 \times 10^{-4} {\rm s}^{-1}$	87±5		
IV ^a	$k_{\rm II} = 0.38 \text{ L mol}^{-1} \text{ s}^{-1}$	47±2		

^a T = 323 K.



quinonimine, the latter being reduced to aminophenol thus explaining the observed kinetics.

From the rate constants of thermal transformation of compounds I-IV measured over a range of temperatures we calculated the activation energy of the process (Table 1).

The studied quinonimines were weakly sensitive to UV and visible light irradiation. The presence of phenoxazine moiety in the molecule could lead to its photochromism [3]. Indeed, under visible light irradiation, yellow-green solutions of quinonimines I-III, partially transformed at preliminary heating (and thus containing their 4aH-phenoxazine derivatives) turned into initial red-violet color. After 5-7 min of irradiation, electron absorption spectra of the solutions were identical to those of the starting quinonimines. Heating of the irradiated solutions induced repeated formation of the 4aH-phenoxazine derivatives and restoration of yellow-green coloration. Hence, the observed heat- and light-induced transformations of compounds I-III in the solution were reversible. The underlying mechanism was thermal ring closure of Zisomer of quinonimine to form 4aH-phenoxazine cycle and subsequent photoinduced ring opening (Scheme 3).

The loss of compounds **I** and **III** after 5 cycles of thermal and phototransformations was 8.0 and 16.7%, respectively.

Kinetics of photolysis of 4a*H*-phenoxazine derivative of quinonimine was studied using compound I as an example; the compound was exposed to 405 nm irradiation with the intensity of $(5-113) \times 10^{17}$ quant L⁻¹ s⁻¹ (Fig. 4). The reaction order was close to unity, and the quantum yield was 0.95 independently of irradiation intensity.

Additionally, we performed quantum-chemical simulation to access the ground state energy of E- and Zisomers of the studied compounds **I–IV** as well as of the corresponding 4a*H*-phenoxazines. Data collected in Table 2 show that the energy of Z-isomers of quinonimines is significantly higher than that of their E-isomers, however being lower than that of the 4a*H*- phenoxazines (products of heat-induced transformation). Disregarding the entropy factor, the energy difference should result in the equilibrium constant of E-quinonimine transformation into phenoxazines of 10^2-10^4 at room temperature; that was consistent with the experimental findings. The reverse process is possible only upon external energy supply (for instance, under irradiation). Noteworthily, the energy difference between *tert*-butyl derivative **IV** and the corresponding phenoxazine was lower than in the cases of **I–III**.

EXPERIMENTAL

Quinonimines **I–IV** were prepared as described in [1, 4], and their structures were confirmed by IR and NMR spectroscopy. The solvents of chemically pure grade were purified and dried as described in [5]. Air was removed from the reaction mixtures by repeated freezing under a reduced pressure.

Heat- and light-induced transformations were studied in evacuated ampules equipped with Teflon valves and quartz windows. Photolysis was performed using the DRSh-500 mercury lamp equipped with quartz lens and standard set of optical filters. Intensity of the incident radiation was measured with the actinometer based on potassium ferrioxalate [6]. Kinetics of the process was monitored by spectrophotometry (the SF-2000 spectrophotometer, quartz cell, optical path of 0.8 cm).

IR spectra of the products were registered with a Shimadzu IRPrestige-21 instrument (KBr). The specimens were prepared by washing the purified and dry salt with the reaction mixture based on hexane, followed by the solvent distillation under reduced pressure and the cell filling with inert gas.

Chromatomass spectrometry analysis was performed using a DSQ II instrument equipped with quadrupole mass analyzer and the MALDI Bruker microflex LT spectrometer (ion source temperature 230°C, ionization energy 70 eV). Mass spectra of cations were registered at the mass number range of 70–800.

Quantum-chemical simulation of ground state of the quinonimines and their 4a*H*-phenoxazine derivatives was performed using GAUSSIAN 09W software package [7]. Starting geometry was set and the results were presented in GaussView software [8]. The preset geometry parameters of 4*Z*- and 4*E*-isomers of quinonimines bearing various substituents in 2,6 or 2,5



Fig. 4. Photolytic transformation of 4a*H*-phenoxazine derivative **B** of compound **I** ($c_0 = 2.3 \times 10^{-4}$ mol/L, $\lambda = 405$ nm, $I_{0,sp} = 1.23 \times 10^{18}$ quant s⁻¹ L⁻¹; (1) is decay of the starting compound, (2) is accumulation of quinonimine **I**.

positions of the phenyl ring (two *tert*-butyl, two isopropyl, two ethyl, or two methyl) as well as of their 4a*H*-phenoxazine derivatives were optimized by the DFT method. Hybrid B3PW91 functional in the 6-31G (d) basis set was used, accounting for *d*-polarization functions. All simulations were performed for isolated molecules.

Output files of GAUSSIAN package contained electron energy of the molecules in Hartree units; that information was used to compute energy difference between Z- and E-isomers of quinonimines and their 4aH-phenoxazines in kJ/mol.

Table 2. Energy of ground states of quinonimines I-IV (*E*and *Z*-isomers) and of products of their heat-induced transformations

Compound	Ι	П	Ш	IV
Energy difference between Z- and E-isomers, kJ/mol $[E(Z) > E(E)]$	5.683	6.313	6.532	9.308
Energy difference between the <i>Z</i> -isomer and the phenoxazine, kJ/mol	20.788	27.336	25.487	12.866
Energy difference between the <i>E</i> -isomer and the phenoxazine, kJ/mol	15.104	21.023	18.955	3.558

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