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Photodecomposition of Substituted *o*-Benzoquinones in Saturated Hydrocarbons: I. Kinetic Relations

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Abstract — Kinetic relations holding in photodecomposition of substituted *o*-benzoquinones were determined, and primary photodecomposition products were identified. Photochemical transformations of *o*-benzoquinones in saturated hydrocarbons were presumed to follow two pathways: decarbonylation and reduction. The first of these is favored by the presence of electron-donor substituents in the quinoid ring.
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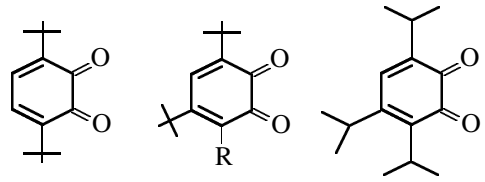
Irradiation of quinones with ultraviolet or visible light gives rise to their numerous transformations as a result of electron transitions in the reactive carbonyl groups [1]. Most publications on this topic deal with photoinduced reactions of quinones with such compounds as alcohols, ethers, amines, alkenes, and alkynes [2]. Vol'eva et al. [3] showed that irradiation of 3,6-di-*tert*-butyl-1,2-benzoquinone in benzene results in its decarbonylation with formation of 2,5-di-*tert*-butylcyclopentadienone. Cyclopentadiene derivatives are widely used both as ligands in the synthesis of metal coordination compounds and in fine organic synthesis [4]. Therefore, it seemed to be important to study the photolysis of substituted *o*-benzoquinones with the goal of elucidating kinetic relations holding in their photochemical transformations and estimating the effect of substituents on the yield of the corresponding cyclopentadienones.

As model substrates we used sterically hindered *o*-benzoquinones **I**–**V** having various donor and acceptor groups.



I **II–IV** **V**

R = H (**II**), Cl (**III**), NO_2 (**IV**).

In the electronic absorption spectra of compounds **I**–**V** we observed two maxima at λ ~400 (π–π* transition in the carbonyl groups) and ~600 nm (*n*–π* transition [5]), the first of these being more intense by approximately two orders of magnitude (Table 1).

Irradiation of dilute solutions of *o*-benzoquinones **I**–**V** in nonane at λ 405 nm led to decrease in the intensity of the absorption maximum at λ ~400 nm in the electronic spectra, and one or several isobestic points appeared in the UV region as photolysis products accumulated in the solution. The kinetic curves for photolysis of all compounds **I**–**V** are reduced to straight lines in semilog coordinates up to a conversion of ~70%. The consumption of *o*-benzoquinones in the photochemical reaction is of first order with respect to the initial substrate concentration, as follows from the slopes (0.91–0.96) of the linear log dependences of the rate of transformation of *o*-benzoquinones upon their concentration in dilute solution.

In the concentration range corresponding to low optical densities ($D \le 0.1$), the rate of photodecomposition of compounds **I**–**V** is linearly related to the initial

Table 1. Absorption maxima in the electronic spectra of solutions of *o*-benzoquinones **I**–**V** in nonane

Comp. no.	π–π* Transition		*n*–π* Transition	
	λ, nm	ε, $l\,mol^{-1}\,cm^{-1}$	λ, nm	ε, $l\,mol^{-1}\,cm^{-1}$
I	400	2660 ± 30	600	49.3 ± 1.2
II	385	2040 ± 50	600	32.2 ± 1.6
III	420	2240 ± 50	570	58.4 ± 0.6
IV	400	2300 ± 20	570	42.0 ± 0.4
V	410	2100 ± 20	590	49.8 ± 0.1

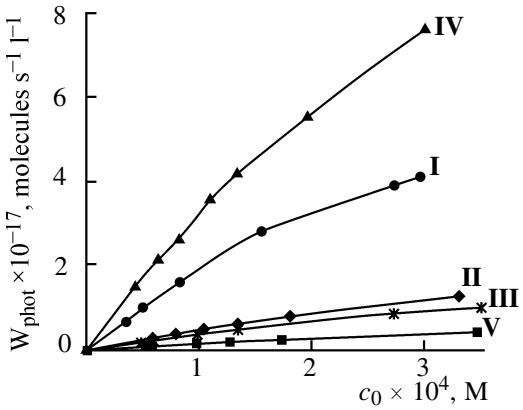


Fig. 1. Plots of the initial rate of photolysis of *o*-benzoquinones **I**–**V** versus initial concentration; temperature 293 K, $I_{0,sp} = 2.37 \times 10^{19}$ quantum s^{-1} l^{-1}.

concentration. At higher concentrations ($D > 1$), deviations from linearity are observed due to increased absorption (Fig. 1). The quantum yields (φ) do not depend on the initial concentration of **I**–**V** in the range from 0.3×10^{-4} to 3.5×10^{-4} M (298 K).

Compound no.	Quantum yield $\varphi \times 10^2$ [a]	Quantum yield $\varphi \times 10^2$ [b]
I	2.81 ± 0.09	2.76 ± 0.04
II	1.03 ± 0.02	1.02 ± 0.01
III	0.76 ± 0.02	0.74 ± 0.01
IV	5.64 ± 0.06	5.64 ± 0.03
V	0.31 ± 0.01	0.32 ± 0.01

[a] $I_{0,sp} = 2.37 \times 10^{19}$ quantum s^{-1} l^{-1}; $c_0 = (0.3–3.5) \times 10^{-4}$ M.
[b] $I_{0,sp} = (0.2–2.8) \times 10^{19}$ quantum s^{-1} l^{-1}; $c_0 = 3.0 \times 10^{-4}$ M.

Photolytic transformations of the examined *o*-benzoquinones in saturated hydrocarbons are accompanied by evolution of carbon(II) oxide. However, the yield of CO depends on the substrate structure.

Compound no.	Yield of CO, mol per mole of quinone
I	1.00 ± 0.07
II	0.93 ± 0.08
III	0.53 ± 0.05
IV	~0.01
V	0.52 ± 0.04

Our results suggest that decarbonylation is the main primary photochemical process for compounds **I** and **II** and that the contribution of decarbonylation pathway to the transformation of quinone **IV** is minor. Taking into account that quinones in the excited triplet n,π^* state are strong hydrogen acceptors [1, 6], the second quite probable transformation pathway may be photochemical reduction leading to phenol ethers.

In keeping with the above experimental kinetic data and structure of the primary photolysis products, a probable scheme of photodecomposition of quinones **I**–**V** can be represented as follows.

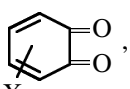
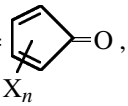
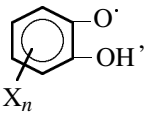
$$Q \xrightarrow{h\nu} {}^1Q^* \longrightarrow {}^3Q^*, \quad (1)$$

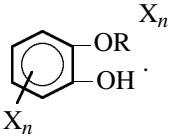
$${}^3Q^* \longrightarrow Q + h\nu_1, \quad (2)$$

$${}^3Q^* + RH \longrightarrow Q + RH, \quad (3)$$

$${}^3Q^* \longrightarrow P_1 + CO, \quad (4)$$

$${}^3Q^* + RH \longrightarrow [Q^{\cdot}H,\ R^{\cdot}] \longrightarrow RQH, \quad (5)$$

Q =  , P_1 =  , RH is solvent (saturated hydrocarbon), $Q^{\cdot}H$ =  ,

RQH =  .

Initially, *o*-benzoquinone molecule takes up a quantum of light ($h\nu$) and is excited to the singlet π,π^* state; the subsequent 100% intersystem crossing gives the triplet n,π^*-state [7] [reaction (1)]. Deactivation of the excited quinone molecule ($^3Q^*$) may be achieved through emission of a quantum of light ($h\nu_1$) whose energy is lower than that of the exciting irradiation ($h\nu_1 < h\nu$) [reaction (2)]. Deactivation is also possible via collision with solvent molecules [reaction (3)]. Finally, the excited molecule may undergo decomposition with elimination of carbonyl group [reaction (4)] or abstraction of hydrogen from solvent molecule [reaction (5)]. By applying the quasistationary concentration principle to excited molecules $^3Q^*$, we obtained an expression for the rate of the process [Eq. (6)].

$$W_{phot} = \frac{I_{0,sp}(1 - 10^{-\varepsilon_\lambda l[Q]})(k_4 + k_5[RH])}{k_2 + k_3[RH] + k_4 + k_5[RH])}. \quad (6)$$

The rate of excitation is linear in the substrate concentration when the latter is low [$D \le 0.1$), Eq. (7)].

$$W_0 = I_{0,sp}(1 - 10^{-\varepsilon_\lambda l[Q]}) = 2.3 I_{0,sp} \varepsilon_\lambda l[Q]. \quad (7)$$

Equation (6) is thus transformed into Eq. (8):

$$W_{phot} = \frac{2.3 I_{0,sp} \varepsilon_\lambda l(k_4 + k_5[RH])[Q]}{k_2 + k_3[RH] + k_4 + k_5[RH])} = k_{ap}[Q]. \quad (8)$$

Here

$$k_{ap} = \frac{2.3I_{0,sp}\varepsilon_\lambda l(k_4 + k_5[RH])}{k_2 + k_3[RH] + k_4 + k_5[RH]} .$$

The quantum yield φ in the photochemical transformation of *o*-benzoquinones is given by Eq. (9).

$$\varphi = \frac{W_{phot}}{I_{a,sp}} = \frac{k_4 + k_5[RH]}{k_2 + k_3[RH] + k_4 + k_5[RH])} = \text{const.} \quad (9)$$

The proposed scheme is well consistent with the observed experimental relations. The apparent rate constants for the photochemical transformations of *o*-benzoquinones **I**–**V** were calculated from the slope of the linear part of the concentration dependences. Using the obtained values and taking into account molar absorption coefficients at the exciting wavelength, we can estimate on a qualitative level the reactivity of quinones **I**–**V** in the examined photochemical processes (Table 2).

The apparent decarbonylation rate constants (k_{ap}^{CO}) were calculated as the product of the yield of CO and k'_{ap}; they showed a correlation with the Hammett constants σ of substituents in the quinoid ring [8] (Fig. 2). The correlation was drawn using 3,5-di-*tert*-butyl-1,2-benzoquinone as reference. The reaction series does not include 3,4,6-triisopropyl-1,2-benzoquinone, for more than one substituent in its molecule differs from those in the reference molecule.

The existence of a correlation between the rate constants for photolytic decarbonylation of *o*-benzoquinones and Hammett constants σ provides an indirect proof for the general character of the scheme proposed for the photolysis of *o*-benzoquinones in saturated hydrocabons. The negative value of ρ indicates that donor substituents (*tert*-butyl groups) [9] favor decarbonylation process and that acceptor substituents (such as chlorine atom and nitro group) increase the contribution of the photochemical reduction pathway.

EXPERIMENTAL

Nonane for photochemical studies and spectrophotometric measurements was purified and dried according to the standard procedure [8] and was then distilled, a fraction with bp 149–151°C (150.7°C [10]) being collected.

The electronic absorption spectra of solutions of *o*-benzoquinones **I**–**V** in nonane were recorded on an SF-46 spectrophotometer using standard 1.0-cm quartz cells. As irradiation source we used a DRSh-500 high-pressure mercury lamp placed into a water-cooled metal jacket. The light beam was focused with a quartz lens and passed through a ZhS-10 light filter to isolate light with λ 405 nm. For kinetic measurement, solutions of *o*-benzoquinones in nonane were deaerated by repeated freeze–thaw cycles under reduced pressure, transferred into a 0.549-cm plane–parallel quartz cell using Teflon valves, and exposed to irradiation for a definite time. The kinetics of the process were monitored by spectrophotometry, following variation of the optical density at the absorption maximum (λ ~400 nm). The incident light intensity was measured with a standard $K_3Fe(C_2O_4)_3$-based chemical actinometer [11].

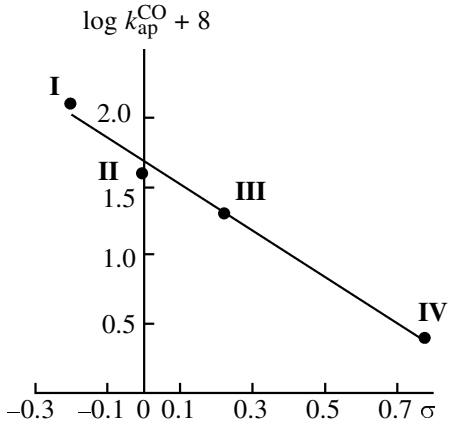


Fig. 2. Correlation between the apparent rate constants of decarbonylation of *o*-benzoquinones **I**–**V** and Hammett substituent constants σ.

The yield of carbon(II) oxide was determined by gas chromatography using a Tsvet-104 chromatograph equipped with a thermal conductivity detector and a

Table 2. Apparent first-order rate constants for the photolysis of *o*-benzoquinones ($I_{0,sp} = 2.37 \times 10^{19}$ quantum s^{-1} l^{-1}; 293 K)

Comp. no.	$k_{ap} \times 10^4$, s^{-1}	ε_λ, $l\,mol^{-1}\,cm^{-1}$	$k'_{ap} \times 10^7$, [a] s^{-1}	$k_{ap}^{CO} \times 10^7$, s^{-1}
I	32.8 ± 0.7	2620 ± 40	12.5 ± 0.6	12.5 ± 0.6
II	8.3 ± 0.2	1830 ± 70	4.2 ± 0.2	3.9 ± 0.2
III	6.8 ± 0.1	1970 ± 30	3.4 ± 0.1	2.0 ± 0.1
IV	54.4 ± 1.9	2200 ± 40	24.8 ± 1.2	0.25 ± 0.02
V	2.9 ± 0.1	2090 ± 20	1.4 ± 0.1	0.70 ± 0.04

[a] The rate constants k'_{ap} were calculated as the ratio of k_{ap} to the molar absorption coefficient at λ 405 nm.

1500 × 2.5-mm glass column packed with NaX 5 Å; oven and detector temperature 30°C; detector bridge current 250 mA; carrier gas helium, flow rate 40 ml min^{-1}.

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