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Photochemical Reactions of Organomercury Compounds in Organic Solvents

V. L. Ivanov, G. A. Artamkina, and A. L. Buchachenko

Department of Chemical Kinetics
e-mail: ivanov@photo.chem.msu.ru

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Abstract—The quantum yields of photolysis of organomercury compounds in different organic solvents have been measured. It was shown that the quantum yields of photolysis of nitro derivatives of mercury compounds and the symmetric (methylnaphthyl)mercury compound are equal to unity. The photolysis of halo derivatives of benzylmercury proceeds with lower quantum yields as compared with photolysis of analogous dibenzylmercury derivatives. The quantum yields of photolysis of organomercury compounds are almost independent of the solvent.

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Mercury is widespread in nature and is a highly toxic environmental pollutant. Its environmental mobility is due to the high sensitivity of mercury compounds to light and their redox processes. In photolysis of bis(*p*-trifluoromethlybenzyl)mercury, the magnetic isotope effect (MIE) for mercury nuclei was observed [1]. Noteworthy are mercury isotope anomalies observed in biological objects, in particular, in fish accumulating mercury from different aquatic systems [2]. It cannot be ruled out that the change in the mercury isotope distribution is associated with photochemical [1] and biochemical processes [3]. The use of organomercury compounds for detecting the MIE requires a preliminary study of their photochemistry, i.e., determination of photolysis quantum yields in organic solvents, which is the aim of this work.

EXPERIMENTAL

Organomercury compounds were synthesized and purified as described in [4]. The extinction coefficients of the synthesized compounds were determined (table).

Solutions placed in 10 × 10 quartz cells were irradiated with light from a DRSh-500 mercury lamp equipped with light filters passing the mercury lines at 313 and 365 nm, as well as with a BS-3 light filter, which absorbs the emission of the initial compound at $\lambda < 310$ nm. The BS-3 light filter was used for cutting off the mercury lamp radiation at $\lambda < 270$ nm. The absorbed light dose was determined from the ratio of the mercury line intensities in the pass band of the BS-3 light filter, actinometry of the mercury line at 365 nm [5], the optical densities of a solution, and the irradiation time. When the samples were irradiated with light from the mercury lamp with the use of a light filter for 313 nm, which also passes the mercury lines at 303 and 297 nm, the absorbed light dose was calculated from the fraction of light of each line, the optical density of a solution at the corresponding wavelength, and the overall light intensity passed by the light filter, which was determined by an actinometer. The quantum yields of photochemical reactions were calculated from the data on changes in the absorption spectra during photolysis and from the absorbed light dose with the use of the Mathcad 2001i program.

Absorption spectra were recorded on a Shimadzu 2102PC spectrophotometer.

RESULTS AND DISCUSSION

In photolysis of organomercury compounds on organic solvents, the initial stage is the rupture of the C–Hg bond. The photoreaction products are metallic mercury and organic compounds generated in dark reactions of nascent radicals. Photolysis of dialkyl- and diarylmercury yields dialkyl and diaryl compounds, as well as the products of the reaction of radicals with hydrocarbon solvents [4, 6]. The photochemistry of dibenzylmercury derivative has been poorly studied. It is only known that photolysis leads to the products of dimerization of benzyl radicals and metallic mercury. The photolysis of organomercury compounds in halogen-containing solvents (CCl_4, $CHCl_3$) yields chlorides of organomercury compounds. It is worth noting that the quantum yields of photolysis of organomercury compounds in solutions are unknown; the exceptions are diphenylmercury [7] and bis(naphthyl-1-methyl)mercury, for which photolysis was studied in different solvents [8].

The photolysis of dibenzylmercury derivatives is accompanied by a change in the absorption spectra of solutions; as a rule, isosbestic points are observed (fig-

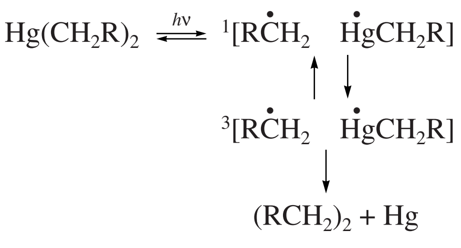
Quantum yields of photolysis of organomercury compounds

Compound, $\varepsilon(\lambda_{max})$, $M^{-1}\ cm^{-1}$*	Solvent	λ_{max}, nm	Light filter	Φ**
Bis-(*p*-chlorobenzyl)mercury, 20000	$CHCl_3$	268	BS-3	0.67
	CCl_4	268	BS-3	0.8
	Heptane	262	BS-3	0.7
Bis-(*m*-fluorobenzyl)mercury, 20300	$CHCl_3$	259	BS-3	0.55
	Heptane	255	BS-3	0.68
	CH_3CN	260	BS-3	0.5
Bis-(*p*-trifluorobenzyl)mercury, 20500	$CHCl_3$	271	BS-3	0.64
	Heptane	265	BS-3	0.44
	i-PrOH	271	BS-3	0.4
p-Nitrobenzylphenylmercury, 7000	$CHCl_3$	336	365	1.0
	Benzene	333	365	1.0
	MeOH	334	365	1.0
	EtOH	336	365	1.0
p-Nitrobenzylmercury bromide, 17000	$CHCl_3$	302	313	0.55
	Benzene	304	313	0.6
p-Nitrobenzylmercury iodide, 20000	$CHCl_3$	307	313	0.62
	Benzene	309	313	0.7
Ethyl *p*-iodophenyl-α-bromomercuryacetate, 16000	$CHCl_3$	266	313	0.1
	Heptane	265	BS-3	0.2
Bis(naphthyl-1-methyl)mercury, 17500	$CHCl_3$	329.5	313	1.0
	CCl_4	329.5	313	1.0
	Benzene	329.5	313	1.0
	Heptane	329.5	313	1.0

* The extinction coefficients of organomercury compounds were determined with an accuracy of 5%.

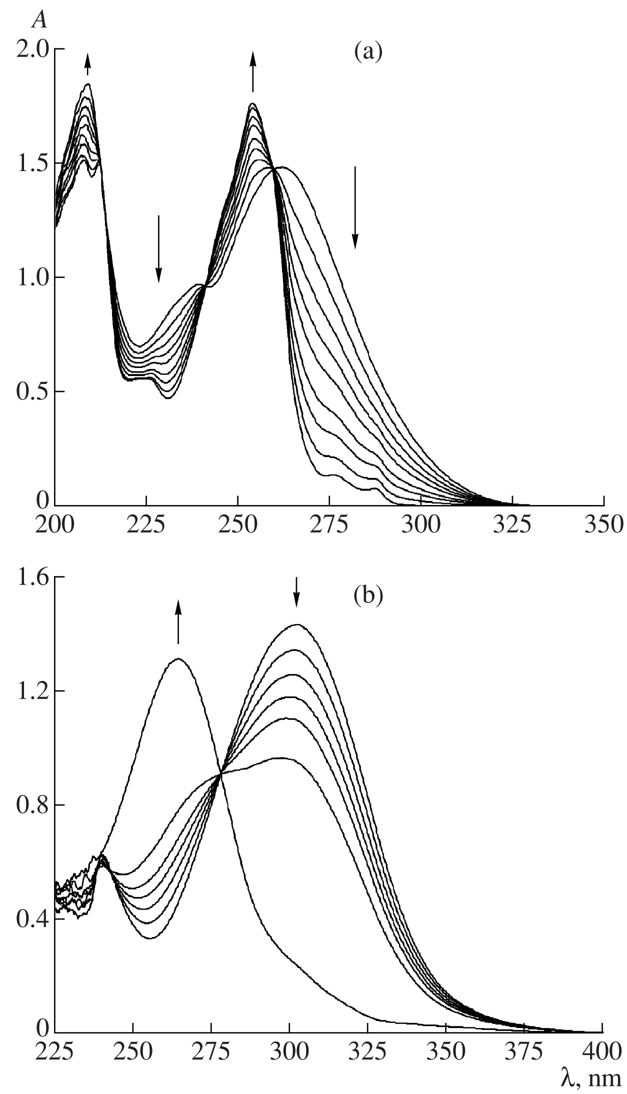
** The quantum yields of photolysis were determined with an accuracy of 10%.

ure), which is evidence that only one reaction product is formed. For photolysis in alcohols, isosbestic points are absent since the benzyl radicals react with an alcohol. In the course of photolysis, the ratio of the dimerization products to the products of elimination of the hydrogen atom from an alcohol changes. At high organomercury concentrations, their photolysis is accompanied by deposition of metallic mercury as a gray precipitate. The quantum yields of photolysis of the organomercury compounds are summarized in the table. Upon the excitation of dibenzylmercury derivatives, the dissociation of the C–Hg bond can take place in both the singlet and triplet states. Organomercury compounds do not fluoresce, which is due to a high probability of bond dissociation in the excited singlet state, as well as to intersystem crossing to the triplet state, since mercury is a heavy atom. The dissociation of the singlet excited state in a solvent yields a singlet radical pair, which can either recombine to form the initial product or undergo spin conversion to give a triplet radical pair. In turn, the triplet radical pair either undergoes spin conversion to again form the singlet radical pair, which recombines into the initial molecule, or dissociates into free radicals. Then, $^{\bullet}HgCH_2R$ radical decomposes with elimination of the mercury atom. The C–Hg bond dissociation energy in the radical is much smaller (~30–40 kJ/mol [9]) than the C–Hg dissociation energy of the initial molecule (~230–250 kJ/mol [10]). The benzyl radicals $^{\bullet}CH_2R$ recombine to form a product (Scheme 1).



Scheme 1.

The photolysis quantum yields for halides of organomercury compounds are lower than the quantum yields of the corresponding dibenzylmercury deriva-



Change in the absorption spectra of (a) bis(*p*-chlorobenzyl)mercury in heptanes on irradiation with light of a DRSh-500 mercury lamp with a BS-3 light filter 5, 10, 15, 20, 30, 40, 60, and 120 s after the onset of photolysis and (b) *p*-nitrobenzylmercury in $CHCl_3$ on irradiation with a filter passing the mercury line at 313 nm 5, 10, 15, 20, 30, and 270 s after the onset of photolysis.

tives, which is also due to different C–Hg bond energies in the salts and dibenzylmercury derivatives. In photolysis of bis(naphthyl-1-methyl)mercury in CCl_4, the product of the photoreaction decomposes upon irradiation with the quantum yield 0.1. The ultimate product of its photolysis is identical to the product of photolysis of the initial compound in heptanes. Thus, our findings demonstrate that electron-accepting substituents in the aromatic ring lead to high quantum yields of the photodecomposition of dibenzylmercury derivatives. Benzylmercury halide derivatives are photolyzed with lower quantum yields as compared to the corresponding dibenzylmercury derivatives. The quantum yields of photolysis of organomercury compounds are almost independent of the solvent.

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