Journal of Organometallic Chemistry, 292 (1985) 335–341
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PARAMAGNETIC ORGANOMERCURY COMPLEXES OF QUINONES: AN ESR STUDY OF ˙TQHgR RADICALS (TQ = benzo[2,1-*b*;3,4-*b*′]dithiophen-4,5-dione)

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(Received March 5th, 1985)

Summary

The ESR spectra of the paramagnetic species produced by photoreaction of benzo[2,1-*b*;3,4-*b*′]dithiophen-4,5-dione with a number of organomercurials, RHgR, have been recorded. The spectral parameters and the temperature dependence of the ^{199}Hg coupling constants are consistent with a structure of the adducts in which the Hg atom is bound to both carbonyl oxygens.

Introduction

The thermally or photolytically induced homolytic cleavage of organomercurials, HgR_2 (R = alkyl or aryl), is a well known process leading to $R^{\cdot}$ radicals via either a one step (reaction 1) or a two step (reactions 2, 3) mechanism [1].

$$R_2Hg \rightarrow 2\ R^{\cdot} + Hg \qquad (1)$$

$$R_2Hg \rightarrow R^{\cdot} + {}^{\cdot}HgR \qquad (2)$$

$$^{\cdot}HgR \rightarrow R^{\cdot} + Hg \qquad (3)$$

In a similar fashion $(R_3Si)_2Hg$ and $(R_3Ge)_2Hg$ are used as sources of silyl and germyl radicals respectively [2–6].

On the other hand, in the presence of compounds with pronounced electron affinity organomercurials can react via a charge-transfer mechanism leading to labile organomercurial radical cations, $R_2Hg^{+\cdot}$, which subsequently fragment into RHg^+ and $R^{\cdot}$ radicals; the formation of the latter species has been confirmed by spin trapping experiments by means of a suitable scavengers, such as PBN [7].

0022-328X/85/$03.30

In the reactions between some quinones and organomercurials, it was possible to characterize by ESR spectroscopy the species RHgQ$^{\cdot}$ resulting from trapping of the HgR fragment by the quinone [8,9]. Although a charge-transfer mechanism was thought to be operating also in these cases (reactions 4–6),

$$Q + HgR_2 \rightarrow Q^{-\cdot} + R_2Hg^{+\cdot} \qquad (4)$$

$$R_2Hg^{+\cdot} \rightarrow RHg^+ + R^{\cdot} \qquad (5)$$

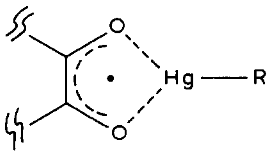
$$Q^{-\cdot} + {}^{+}HgR \rightarrow {}^{\cdot}QHgR \qquad (6)$$

homolytic cleavage of a carbon–mercury bond followed by addition of RHg$^{\cdot}$ to the quinone (reactions 3, 7) could not be ruled out on the basis of the available data [9].

$$R_2Hg \rightarrow R^{\cdot} + {}^{\cdot}HgR \qquad (3)$$

$$RHg^{\cdot} + Q \rightarrow {}^{\cdot}QHgR \qquad (7)$$

The persistence of the $^{\cdot}$QHgR radicals is strongly dependent on the nature of the quinone and of the solvent used for the reaction. On the basis of their ESR spectral parameters these radicals have been assigned the general structure I, where the

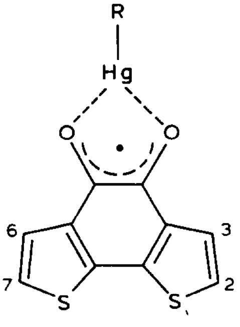


(I)

mercury atom is coordinated by both the quinone oxygens; this can be taken as an indication of sp^2 hybridization at mercury, which can be achieved by promotion of a $5d$ electron in a $6p$ orbital, but coordination may also occur by interaction of an oxygen lone pair and the in plane vacant $6p$ orbital of a sp hybridized mercury. Indeed, the ESR data for radicals I show that symmetric quinones do not lose their symmetry upon complexation; this retention of symmetry, however, may be only apparent and result from a rapid exchange of the mercury atom between the two oxygens (i.e. averaging of two equal unsymmetrical structures where Hg is bound to only one oxygen atom). On the other hand, such a fluxional process should be slowed down by lowering the temperature, giving rise to linewidth alternation effects in the ESR spectra (see for example the radical adducts $^{\cdot}$TQSiPh$_3$ and $^{\cdot}$TQGePh$_3$ obtained by reaction of TQ with triphenylsilyl and triphenylgermyl radicals, respectively [10]); while no such effects have been evidentiated in previous studies [8,9], thus suggesting that the mercury atom is equally bound to the two carbonyl oxygens, a migration process characterized by a very low activation energy cannot be ruled out.

In order to gain further insight in the structure and properties of these radicals, we have carried out an ESR investigation of the paramagnetic species resulting from the reaction of benzo[2,1-*b*;3,4-*b*′]dithiophen-4,5-dione (TQ) with several organomercurials, namely dimethyl- (DMM), diethyl- (DEM), dibenzyl- (DBM), diphenyl- (DPM), di-2-furyl- (D2FM), di-3-furyl- (D3FM), di-2-thienyl- (D2TM), and di-3-thienyl-mercury (D3TM) in t-butylbenzene and in the more polar THF over a wide temperature range. TQ was chosen because of the rather high persistence of the resulting ˙TQHgR radicals, and for the simplicity of their spectra. In fact, photolysis inside the cavity of an ESR spectrometer of solutions of TQ and an organomercurial led to the detection of strong ESR signals. The quality of the spectra, which could be detected over a wide temperature range, was dependent on the temperature, but, although stronger spectra were often detected well above room temperature, the increase in intensity was usually paralleled by an undesirable loss of resolution.

In all cases the spectra consisted of a triplet (1/2/1, ca. 0.78–0.82 G) of triplets (1/2/1, ca. 0.18–0.20 G) due, respectively to protons 2,7 and protons 3,6 of the quinone; an additional 1/2/1 triplet splitting (0.18 G) due to two methylenic protons was resolvable in the ˙TQHgBenzyl and ˙TQHgEthyl adducts. Evidence that the observed radicals indeed contain mercury comes from their very low *g*-factors (2.0006–2.0010), a peculiarity of ˙QHgR radicals [8], and from the presence of satellite lines on the two wings of the main spectrum due to one ^{199}Hg nucleus ($I = 1/2$, natural abundance 16.86%); in contrast no lines due to ^{201}Hg ($I = 3/2$, natural abundance 12.24%) could be observed. Our failure to detect ^{201}Hg satellites is consistent with previous reports [11] on mercury-containing radicals, and can possibly be attributed to quadrupolar relaxation. We therefore assign to the ˙TQHgR radicals the general structure II.



(II)

Although the electron transfer mechanism (reactions 4–6) still appears to be the most likely route to ˙TQHgR radicals, the aforementioned increase in intensity of the ESR signals with increasing temperature observed for some of these species is probably due to more rapid fragmentation of the thermally labile organomercurials, leading to higher concentrations of ˙HgR and hence of the ˙TQHgR adducts (reactions 3 and 7).

We have also run some CIDEP experiments with different organomercurials, in an attempt to evidentiate a possible role of the photoexcited triplet state of the quinone as initiator. The formation of the ˙TQHgR species could also conceivably occur via an S_H2 displacement of an ˙R radical from mercury by attack of the photoexcited quinone (see reactions 8 and 9):

$$\mathrm{TQ} \xrightarrow{h\nu} \mathrm{TQ}^{\star} \tag{8}$$

$$\mathrm{TQ}^{\star} + \mathrm{HgR_2} \rightarrow {}^{\cdot}\mathrm{TQHgR}^{\star} + {}^{\cdot}\mathrm{R} \tag{9}$$

However, none of the observed radicals appeared to be polarized, and no useful indications could be derived from the CIDEP experiments.

It is evident from the data listed in Table 1 that the nature of the group R in the HgR fragment does not affect the spin density distribution on the quinonoid fragment of ˙TQHgR. Instead, the more significant variations are experienced by the mercury hyperfine splitting constant, which is also markedly dependent on the solvent and on the temperature.

The magnitude of the Hg coupling constant and its temperature dependence can be used to establish the structure of radicals II unambiguously. The metal atom is "β" to a radical centre, and its splitting is expected to show a strong angular dependence. In particular, it should be large and positive when the bond between Hg and the atom "α" to the radical centre eclipses the singly occupied MO, maximizing hyperconjugative interactions. On the other hand, indirect spin polarization due to "σ–π" exhange, especially effective when the "β" atom lies in the molecular plane, will lead to small and negative metal coupling constants.

If the mercury atom resides between the two oxygens and in the proximity of the molecular plane, the latter mechanism can be expected to prevail, and the observed $a(^{199}Hg)$ coupling constant should be negative. Increase in the temperature will result in vibrational excitation, i.e. will enhance the oscillation of the HgR moiety out of the molecular plane, allowing the mercury atom to acquire positive spin density and inducing a net reduction of the observed metal splitting. The negative temperature dependence of $a(^{199}Hg)$ observed for radicals IIe–IIg is therefore

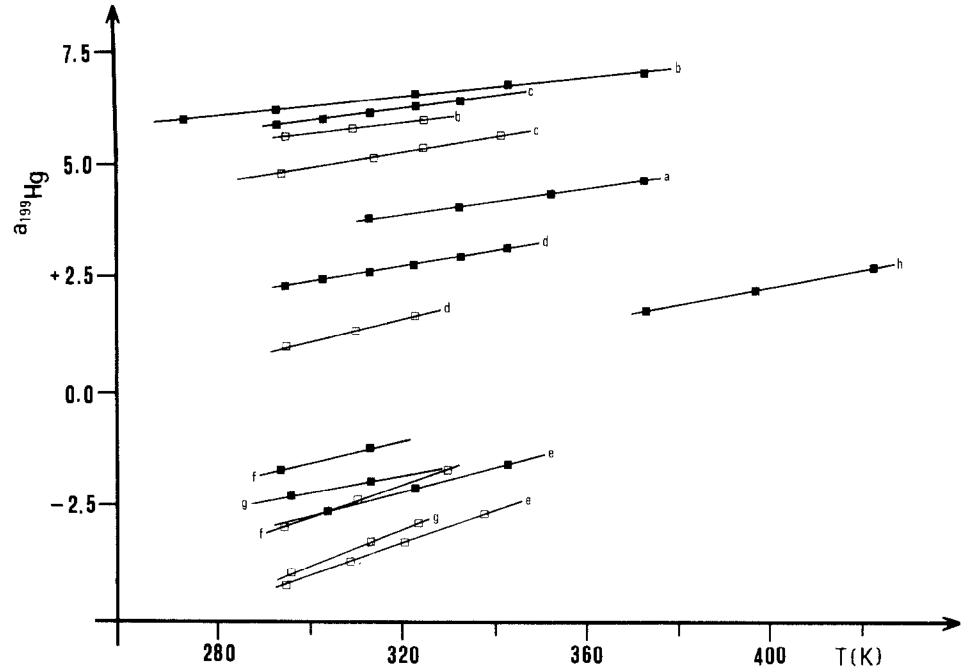


Fig. 1. Temperature dependence of the hyperfine splitting constants $a(^{199}Hg)$ for radical adducts IIa–IIh in t-butylbenzene (full symbols) and in THF (empty symbols).

TABLE 1

ESR SPECTRAL PARAMETERS OF RADICALS ˙TQHgR (IIa–IIh) IN t-BUTYLBENZENE (BB) AND IN THF AT ROOM TEMPERATURE (Coupling constants in Gauss)

Radical	HgR	Solvent	$a_{2,7}$	$a_{3,6}$	a(2H)	g	a(Hg)	da/dT [a]
IIa	DMM	BB	0.81	0.20	–	2.0007	+2.78 [b]	13.8
IIb	DEM	BB	n.r.	0.78	n.r.	2.0010	+5.92	10.4
IIb	DEM	THF	0.16	0.77	0.16	2.0012	+5.51	11.0
IIc	DBM	BB	0.18	0.79	0.18	2.0008	+5.83	13.8
IIc	DBM	THF	0.16	0.77	0.16	2.0009	+4.79	17.0
IId	DPM	BB	0.20	0.80	–	2.0007	+2.31	17.1
IId	DPM	THF	0.19	0.79	–	2.0011	+0.94	22.7
IIe	D2FM	BB	0.20	0.82	–	2.0008	−2.84	27.0
IIe	D2FM	THF	0.19	0.80	–	2.0002	−4.28	37.0
IIf	D3FM	BB	0.20	0.82	–	2.0009	−1.81	25.5
IIf	D3FM	THF	0.18	0.79	–	2.0003	−2.95	33.3
IIg	D2TM	BB	0.20	0.82	–	2.0007	−2.37	20.6
IIg	D2TM	THF	0.18	0.79	–	1.9995	−4.13	40.7
IIh	D3TM	BB	0.20	0.81	–	2.0008	+1.71 [c]	0.18 [d]
IIh	D3TM	THF	0.17	0.78	–	2.0002	1.22	n.m.

[a] mG K^{-1}. [b] T 313 K. [c] T 373 K. [d] in the range 373 to 423 K.

expected. On this basis it would appear that for radicals IIa–IId and IIh the negative spin density induced at the metal through spin polarization is overcome by the positive contribution due to hyperconjugative transfer over the whole of the examined temperature range.

As far as the effect of substitution at mercury is concerned, an examination of Fig. 1 and of the data in Table 1 indicate that ˙TQHgR radicals in which R is an aryl group (IId–IIh) have mercury h.f.s. constants smaller than those for the corresponding radicals IIa–IIc in which R is an alkyl or benzyl group. Although this may be attributed to a partial delocalization of the unpaired electron into the aromatic ring [9], it should be noted that the observed variations of the $a(^{199}\mathrm{Hg})$ splitting upon substitution of the aromatic ring do not parallel their π-delocalizing ability, which is known to increase in the sequence 2-furyl < phenyl < 2-thienyl.

In a recent UPS study [12] of some R_2Hg compounds it has been shown that in D2FM and D2TM there is a significant conjugative interaction from the π_3 orbital of the aromatic group to the empty 6p mercury orbital. The magnitude of this interaction depends on the relative energies of the involved orbitals, being greater for smaller energy gaps, and is therefore expected to decrease upon going from D2FM (furan IP 8.89 eV) [13] and D2TM (thiophene IP 8.87 eV) [13] to DPM (benzene IP 9.24 eV) [14]. The trend observed for $a(^{199}\mathrm{Hg})$ in radicals II upon substitution of the R groups suggests that a similar conjugative interaction may be operative also in radicals IId, IIe, IIg, and, to some extent, also in radicals IIf and IIh, despite the smaller coefficients of the π_3 orbital at the position 3 of the heteroaromatic rings.

A further noticeable feature emerging from the data collected in Table 1 is that for all ˙TQHgR radicals the metal splitting is significantly lower in THF than it is in t-butylbenzene. This can be attributed to solvation of the mercury atom by the more polar ethereal solvent, which makes coordination by the carbonyl oxygens less efficient.

Finally, it may be worthwhile pointing out that although $^{\cdot}$TQHgR radicals may be structurally related to the paramagnetic complexes obtained by reaction of TQ with some metal carbonyls ($^{\cdot}$TQM(CO)$_4$, with M = Mn, Re) [15] and with some Group V organometallic compounds ($^{\cdot}$TQMR$_2$, with M = As, Sb, Bi and R = Ph) [16], in the $^{\cdot}$TQHgR adducts the spin density at the metal atom, as determined by dividing the observed metal coupling by the appropriate A_0 value [17], is only ca. 4×10^{-4}, i.e. an order of magnitude smaller than those in the above mentioned complexes.

Experimental

Benzo[2,1-*b*'3,4-*b*']dithiophen-4,5-dione (TQ) was synthesized as previously described [18]. Most of the organomercurials, viz. dimethyl- (DMM), diethyl- (DEM), dibenzyl- (DBM) and diphenyl-mercury (DPM) were commercially available (Alfa, Merck, Ventron), while di-2-furyl- (D2FM), di-2-thienyl- (D2TM), di-3-furyl- (D3FM), and di-3-thienyl-mercury (D3TM) [19] were prepared by standard methods.

The ESR spectra were recorded on a Bruker ER 200 spectrometer equipped with a NMR gaussmeter (field calibration), a frequency counter (*g*-factor determination), and standard variable temperature devices. A 1 kW Philips high pressure mercury lamp was used as a source of UV light, which was filtered through a cell (5 cm) containing a water solution of $NiSO_4$ (1.14 *M*) and $CoSO_4$ (0.21 *M*) [20] to cut out the infrared component.

The samples consisted of deoxygenated benzene solutions of the quinone containing a small amount of an organomecurial. No improvement of the quality of the spectra could be achieved by degassing the samples via the freeze-thaw technique.

In some instances at the higher temperatures ESR spectra could be detected even before UV irradiation, and, although their intensities were usually strongly enhanced by the UV light, in a few cases prolonged irradiation resulted in a faster disappearance of the ESR signal.

Acknowledgement

The authors are grateful to Mr. G. Bragaglia for his skillful technical assistance.

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