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Abstract

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ARYLMERCURY DERIVATIVES OF NITROSOPHENOLS

Owing to the use of spectral methods of investigation and X-ray structural analysis, the problem of nitrosophenol-quinone oxime tautomerism has now been essentially solved. In the solid state nitrosophenols exist in the quinone oxime form ($^{1-3}$); in solution, for compounds of the benzene series, tautomeric transformation occurs through the intermediate formation of a mesomeric anion ($^{4-9}$).

$$\text{HO-C}_6\text{H}_4\text{-NO} \rightleftharpoons {}^{-}\text{O-C}_6\text{H}_4\text{-NO} \rightleftharpoons \text{O=C}_6\text{H}_4\text{=NO}^{-} + \text{H}^{+} \rightleftharpoons \text{O=C}_6\text{H}_4\text{=NOH}$$

(nitrosophenol form) (mesomeric anion) (quinonoid anion) (quinone oxime form)

In the present work we have investigated the behavior of the arylmercury radical in the nitrosophenol—quinone oxime system. By reaction of arylmercury hydroxides with nitrosophenols, their arylmercury derivatives were obtained according to the general scheme (Table 1):

$$\text{RHgOH} + \text{HA} \rightarrow \text{RHgA} + \text{H}_2\text{O},$$

where HA is a nitrosophenol.

The compounds obtained are brightly colored crystalline substances, insoluble in water. NaOH cleaves them into the corresponding sodium nitrosophenolate and arylmercury hydroxide:

$$\text{RHgA} + \text{NaOH} \rightarrow \text{RHgOH} + \text{NaA}.$$

Consequently, they may have either a benzenoid or a quinonoid structure:

$$\text{RHgO-C}_6\text{H}_4\text{-NO} \quad \text{or} \quad \text{RHgON=C}_6\text{H}_4\text{=O}.$$

It is known that a nitroso group bound to an aromatic nucleus has, in the region 11000—17000 cm^{-1}, a characteristic absorption whose intensity depends little on the substituents in the nucleus and on the solvent (^{10,11}). This has been used to determine the content of the nitroso form in the tautomeric system of nitrosophenol ($^{7-10}$). In addition to tautomerism, a decrease in the intensity of absorption may be caused by partial dimerization of nitroso compounds (^{11,12}). In this case the extinction coefficient depends on concentration. Spectra were recorded for derivatives of nitrosobenzene, nitrosophenols, and their arylmercury derivatives in the region 11000—17000 cm^{-1} in tetrahydrofuran (THF) and other solvents, with cell thicknesses of 10—100 mm (see Table 2 and Fig. 1)*.

In the spectra of nitrosonaphthols, anthraquinone oxime, and their arylmercury derivatives, the maximum of the NO group is absent, which indicates their quinone oxime structure. The spectra of nitrosophenols and their arylmercury derivatives contain the characteristic band of the NO group; its intensity is considerably reduced, depends on the solvent, and does not depend on concentration. The latter indicates the absence of dimerization. It is known that arylmercury compounds are weakly dissociated at the Hg—O bond (^{13}). Therefore, on the basis of the presence in the spectra of arylmercury derivatives of nitrosophenols of absorption of the NO group, the intensity of which is reduced and de-

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* Absorption spectra were recorded on an SFD-1 spectrophotometer in the optical laboratory of the Institute of Organoelement Compounds of the Academy of Sciences of the USSR.

Table 1

RHgR′

R	R	M.p. (decomp.), °C	Yield, %	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.	Hg, % found	Hg, % calc.
4-$(CH_3)_2NC_6H_4$	—ON=p-benzoquinone=O	126 from alcohol	71	38.11; 37.95	38.20	3.28; 3.25	3.17	6.54; 6.76	6.35	45.33; 45.20	45.30
Same	—ON=methyl-substituted p-benzoquinone=O	141 from alcohol	91	39.18; 39.10	39.40	3.40; 3.61	3.50	6.37; 6.19	6.14	43.54; 43.67	43.70
» »	—ON=methyl-substituted p-benzoquinone=O	135 from alcohol	93	39.35; 39.36	39.40	3.41; 3.38	3.50	6.55; 6.38	6.14	44.01; 43.90	43.70

R	R	M.p. (decomp.), °C	Yield, %	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.	Hg, % found	Hg, % calc.
» »	—ON=chloro-substituted p-benzoquinone =O	112 from alcohol	88	35.20; 35.27	35.35	2.91; 2.85	2.72	5.96; 5.85	5.87	41.83; 41.75	41.90
» »	nitroso-naphthoquinone derivative	132 from C_6H_6	64	44.09; 43.97	43.90	3.27; 3.31	3.25	5.85; 5.74	5.70	40.46; 40.83	40.65
» »	naphthoquinone nitroso derivative	158 from alcohol	90	44.05; 43.94	43.90	3.31; 3.29	3.25	5.64; 5.65	5.70	40.68; 40.34	40.65
» »	nitroso-naphthoquinone derivative	156 from C_6H_6	85	44.10; 44.05	43.90	3.28; 3.33	3.25	5.75; 5.81	5.70	40.57; 40.63	40.65
» »	nitroso-anthraquinone derivative	155 from C_6H_6	82	48.47; 48.41	48.60	3.39; 3.27	3.32	5.38; 5.28	5.17	37.17; 37.09	36.95
C_6H_5	—ON=p-benzoquinone =O	137 from C_6H_{12}	92	35.92; 35.87	36.00	2.19; 2.23	2.25	3.30; 3.47	3.50	50.17; 50.23	50.00
4-CH$_3$OC$_6$H$_4$	—ON=p-benzoquinone =O	143 from C_6H_{12}	91	36.41; 36.49	36.32	2.63; 2.50	2.55	3.33; 3.24	3.26	46.42; 46.55	46.50

···depends appreciably on the solvent; one should therefore assume for them, by analogy with the corresponding nitrosophenols, the existence of tautomerism through the stage of formation of a mesomeric anion:

$$\text{OHgR-substituted nitroso form} \rightleftharpoons \text{anion form} \rightleftharpoons \text{quinonoid nitroso anion} + \text{RHg}^{+} \rightleftharpoons \text{quinonoid NOHgR fo}$$

Taking $\varepsilon_{\max}$ as approximately proportional to the content of the nitroso form, the following conclusions may be drawn. Substitution in the nitrosophenol nucleus leads to a decrease in the content of the nitroso form in solution. Arylmercury derivatives are characterized by an increased content of the nitroso form in comparison with the corresponding nitrosophenols, especially in the case of nitroso-*m*-cresol and *o*-chloronitrosophenol. The nature of the arylmercury radical does not appreciably affect the position of the tautomeric equilibrium. The dependence of the tautomeric equilibrium on the solvent is not strictly similar for nitrosophenol and its arylmercury derivative. In contrast to the arylmercury deriv—

···aqueous nitrosophenol, the absorption of the NO group is absent in the spectrum of the nitrosophenolate anion, which indicates its quinone-oxime structure (see Fig. 1). To establish the structure of the arylmercury derivatives in the solid state, their IR spectra and the spectra of methyl ethers of quinone oximes in the region 1400–2000 cm^{-1}* were recorded.

Table 2

Compound	Solvent	ν_{max}, $cm^{-1} \cdot 10^{-3}$	ε_{max}	Compound	Solvent	ν_{max}, $cm^{-1} \cdot 10^{-3}$	ε_{max}
C_6H_5NO	THF	13.2	48	$RHgOC_6H_4NO$-4	$CH_3COOC_2H_5$	13.9	11
4-ClC_6H_4NO	»	13.2	45	Same	$CHCl_3$	14.2	3.2
2-$CH_3OC_6H_4NO$	»	12.8	51	» »	dioxane	13.9	12.5
4-$CH_3OC_6H_4NO$	»	13.6	52	$C_6H_5HgOC_6H_4NO$-4	THF	13.9	15
Same	$CH_3COOC_2H_5$	13.6	49	$CH_3OC_6H_4HgOC_6H_4NO$-4	»	13.9	15.5
» »	$CHCl_3$	13.8	52	$HOC_6H_3(CH_3$-3)(NO-4)	»	13.3	2.7
» »	dioxane	13.6	52	$RHgOC_6H_3(CH_3$-3)(NO-4)	»	13.6	9.9
HOC_6H_4NO-4	THF	13.6	12.5	$HOC_6H_3(CH_3$-2)(NO-4)	»	13.6	1.6
Same	$CH_3COOC_2H_5$	13.8	13	$RHgOC_6H_3(CH_3$-2)(NO-4)	»	13.9	3.0
» »	$CHCl_3$	13.9	2.8	HOC_6H_3(Cl-2)(NO-4)	»	13.6	2.5
» »	dioxane	13.7	7.2	$RHgOC_6H_3$(Cl-2)(NO-4)	»	14.0	13.5

Compound	Solvent	ν_{max}, cm^{-1} · 10^{-3}	ε_{max}	Compound	Solvent	ν_{max}, cm^{-1} · 10^{-3}	ε_{max}
$RHgOC_6H_4NO$-4	THF	14.0	16				

R = 4-$(CH_3)_2NC_6H_4$–

According to the literature data, bands characteristic of the quinone-oxime structure are absorption bands in the region 1520–1580 cm^{-1}, corresponding to vibrations of the C=N or C=C bond, and bands at 1625–1645 cm^{-1}, assigned to the carbonyl group (^{1,2}). In the spectra of the arylmercury derivatives (with the exception of the derivative of 2-oxime of 1,2-naphthoquinone) and of the methyl ethers of quinone oximes, characteristic bands are present in the regions 1550–1590 cm^{-1} and 1620–1660 cm^{-1} (see Table 3). On this basis the arylmercury derivatives in the solid state should be assigned a quinone-oxime structure. In the case of the derivative of 2-oxime of 1,2-naphthoquinone, the question remains open.

Table 3

Compound	ν, cm^{-1}, in powder	ν, cm^{-1}, in $CHCl_3$	Compound	ν, cm^{-1}, in powder	ν, cm^{-1}, in $CHCl_3$
$CH_3ON{=}C_6H_4{=}O$	1585, 1646	–, 1655	$RHgON{=}C_6H_4{=}O$	1592, 1627	1600, 1660
$CH_3ON{=}C_6H_3(CH_3){=}O$	1585, 1645	–, 1656	$NOCH_3$-substituted naphthoquinone oxime ether	1592, 1650	–, 1670
$C_6H_5HgON{=}C_6H_4{=}O$	1573, 1623	–, 1636	naphthoquinone oxime arylmercury derivative	1570, –	1603, –
4-$CH_3OC_6H_4HgON{=}C_6H_4{=}O$	1589, 1627	–, 1636	naphthoquinone oxime arylmercury derivative	1577, 1627	1595, 1632

Compound	ν, cm^{-1}, in powder	ν, cm^{-1}, in $CHCl_3$	Compound	ν, cm^{-1}, in powder	ν, cm^{-1}, in $CHCl_3$
$RHgON{=}C_6H_4{=}O$	1588, 1629	1600, 1634	RHgON=anthraquinone-type structure=O	1585, 1645	1602, 1660
$RHgON{=}C_6H_3(CH_3){=}O$	1592, 1628	1605, 1635			
$RHgON{=}C_6H_3(CH_3){=}O$	1588, 1623	1603, 1638			

R = 4-$(CH_3)_2NC_6H_4$–

* The IR spectra were recorded on a VIKS-M3 spectrograph in the optical laboratory of the Institute of Organoelement Compounds, Academy of Sciences of the USSR.

The presence of the quinone-oxime form in solutions of arylmercury derivatives of nitrosophenols is confirmed by IR spectra. In the IR spectra of solutions of arylmercury derivatives of nitrosophenols in chloroform there is a band of the C=O group in the region of 1620—1670 cm^{-1} and a band of the C=C bond at ~ 1600 cm^{-1}, which is not always manifested because of

Fig. 1. Absorption spectra of nitrosophenols and their arylmercury derivatives in tetrahydrofuran.

Fig. 1. Absorption spectra of nitrosophenols and their arylmercury derivatives in tetrahydrofuran:
(1)–$CH_3OC_6H_4NO$-4,
(2)–$(CH_3)_2NC_6H_4HgOC_6H_4NO$-4,
(3)–KOC_6H_4NO-4,
(4)–HOC_6H_4NO-4,
(5)–$CH_3ON{=}C_6H_4{=}O$,
(6)–$CH_3OC_6H_4NO$,
(7)–[[unclear: structural formula]],
(8)–[[unclear: structural formula]],
(9)–[[unclear: structural formula]],
(10)–[[unclear: structural formula]].

overlap with the intrinsic absorption of $CHCl_3$. Thus, the data obtained show that the arylmercury derivatives of nitrosophenols exhibit a great similarity to the corresponding nitrosophenols, possessing a quinone-oxime structure in the solid state and being tautomeric for the benzene series in solution.

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CITED LITERATURE

1. D. Hadži, *J. Chem. Soc.*, **1956**, 2725.
2. G. E. Philbrook, T. C. Getten, *J. Org. Chem.*, **24**, 568 (1959).
3. C. Romers, C. B. Shoemocker, E. Fischmann, *Rec. trav. chim., Pays-Bas*, **76**, 490 (1957).
4. P. Ramart-Lucas, M. M. Martynoff, *Bull. Soc. chim., France*, **15**, 571 (1948).
5. P. Ramart-Lucas, M. M. Martynoff, *Bull. Soc. chim., France*, **16**, 53 (1949).
6. E. Baltazzi, C. R., **232**, 977 (1951).
7. A. Schors, A. Kraaijeveld, E. Havinga, *Rec. trav. chim., Pays-Bas*, **74**, 1243 (1955).
8. E. Havinga, A. Schors, *Rec. trav. chim., Pays-Bas*, **69**, 457 (1950).
9. A. Burawoy, M. Cais, Y. T. Chamberlain, F. Liversedge, A. R. Thompson, *J. Chem. Soc.*, **1955**, 3727.
10. E. Hertel, F. Lebock, *Zs. phys. Chem.*, **47**, 315 (1940).
11. W. J. Mijs, S. E. Hoekstra, R. M. Ulmann, E. Havinga, *Rec. trav. chim., Pays-Bas*, **77**, 746 (1958).
12. C. K. Ingold, H. A. Pigott, *J. Chem. Soc.*, **125**, 169 (1924).
13. T. D. Wavgh, H. F. Walton, J. A. Laswick, *J. Phys Chem.*, **59**, 395 (1955).

Note: Figure translations are in progress. See original paper for figures.