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AN INVESTIGATION OF ADDUCTS OF ARSONIC ACIDS WITH AMINES BY NUCLEAR QUADRUPOLE RESONANCE OF ^{75}As NUCLEI

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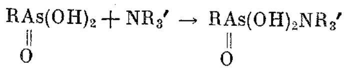
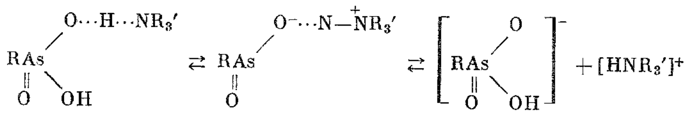
Continuing our research on organoarsenic compounds by nuclear quadrupole resonance (NQR) of ^{75}As [1, 2], we have investigated the ^{75}As NQR spectra of the adducts of arsonic acids with amines of the general formula $RAs(O)(OH)_2NR_3'$. These adducts, which exhibit a wide range of biological activity [3], are of definite practical interest, but as yet the structure of these compounds has not been closely investigated by physicochemical methods. The adducts were synthesized by direct mixing of alcoholic solutions of arsonic acids with amines



$$\underset{\overset{\|}{O}}{RAs}(OH)_2 + NR_3' \rightarrow \underset{\overset{\|}{O}}{RAs}(OH)_2NR_3'$$

According to present ideas [4], the structure of adducts of arsonic acids and amines can be represented as follows



(A) (B) (C)

where (A) is an H complex, (B) is an H complex of ionic type or an ion pair, and (C) are dissociated ions of salt-like form.

We have investigated a wide range of derivatives of arsonic acids with different pK_a values and aliphatic primary and secondary amines with different basicities. Depending on the nature of the initial acids and amines,

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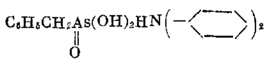
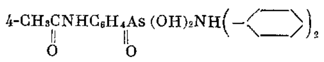
TABLE 1. ^{75}As NQR Frequencies of Arsonic Acids and Their Adducts with Amines

Compound	Formula	ν, MHz	$\Delta\nu = \nu_{ad} - \nu_{ac}$, MHz*
	$C_6H_5\underset{\underset{O}{\|}}{As}(OH)_2$	48,22	
(I)	$C_6H_5\underset{\underset{O}{\|}}{As}(OH)_2H_2NCH_3$	38,63	−9,59
(II)	$C_6H_5\underset{\underset{O}{\|}}{As}(OH)_2HN(CH_3)_2$	35,42	−12,80
(III)	$C_6H_5\underset{\underset{O}{\|}}{As}{\genfrac{}{}{0pt}{}{/OH}{\backslash ONa}}$	42,89 43,30	−5,33 −4,92
	$4\text{-}NH_2C_6H_4\underset{\underset{O}{\|}}{As}(OH)_2$	35,95	
(IV)	$4\text{-}NH_2{-}C_6H_4\underset{\underset{O}{\|}}{As}(OH)_2HN(CH_3)_2$	38,04	2,09
	$2\text{-}NH_2{-}C_6H_4\underset{\underset{O}{\|}}{As}(OH)_2$	49,16	
(V)	$2\text{-}NH_2{-}C_6H_4\underset{\underset{O}{\|}}{As}{\genfrac{}{}{0pt}{}{/OH}{\backslash ONa}}$	49,24	0,08
	$2\text{-}NH_2\text{-}5\text{-}NO_2C_6H_3\underset{\underset{O}{\|}}{As}(OH)_2$	41,15	
(VI)	$2\text{-}NH_2\text{-}5\text{-}NO_2C_6H_3\underset{\underset{O}{\|}}{As}(OH)_2 \cdot HN(CH_3)_2$	42,53	1,38
	$CH_2{=}CHCH_2\underset{\underset{O}{\|}}{As}(OH)_2$	50,90 50,50	
(VII)	$CH_2{=}CHCH_2\underset{\underset{O}{\|}}{As}(OH)_2H_2NCH_2OC_4H_3$	40,920	−9,78†
	$C_6H_5CH_2\underset{\underset{O}{\|}}{As}(OH)_2$	51,18	
(VIII)	$C_6H_5CH_2\underset{\underset{O}{\|}}{As}(OH)_2 \cdot H_2NCH_2OC_4H_3$	40,120	−11,06
(IX)	 $C_6H_5CH_2\underset{\underset{O}{\|}}{As}(OH)_2HN(-\ )_2$	41,92 36,86	−9,26 −14,32
	$4\text{-}CH_3\underset{\underset{O}{\|}}{C}NHC_6H_4\underset{\underset{O}{\|}}{As}(OH)_2$	43,10	
(X)	 $4\text{-}CH_3\underset{\underset{O}{\|}}{C}NHC_6H_4\underset{\underset{O}{\|}}{As}(OH)_2NH(-\ )_2$	37,08	−6,02
	$2\text{-}CH_3\underset{\underset{O}{\|}}{C}NHC_6H_4\underset{\underset{O}{\|}}{As}(OH)_2$	47,02	
(XI)	$2\text{-}CH_3\underset{\underset{O}{\|}}{C}NHC_6H_4\underset{\underset{O}{\|}}{As}(OH)_2H_2NCH_2OC_4H_3$	37,70	−9,32

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*ν_{ad} and ν_{ac} are the resonance frequencies of the adduct and the initial acid, respectively.

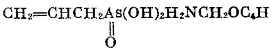
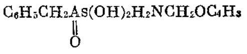
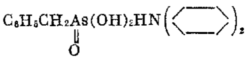
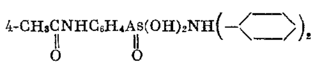
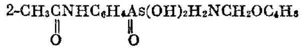
†From mean value of ν_{ac}.

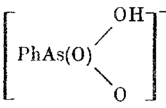
the synthesized adducts may exist in any of three possible forms (A)-(C). Table 1 gives the ^{75}As NQR spectra of the initial acids and their adducts.

On the basis of the possible forms of existence of the adducts of arsonic acids and aliphatic amines it might have been expected that a complex with hydrogen bonds of type (A) must be characterized by small shifts of the resonance frequencies Δν, because the initial arsonic acids are a complex system with intra- and intermolecular H bonds. According to x-ray structural analysis data [5-7], molecules of arsonic acids in the crystalline phase are combined by H bonds into infinite chains, in certain cases mutually cross-linked. This means that the formation of complexes of type (A) must be accompanied by very slight rearrangement of the electron environment of the arsenic nucleus.

Complete proton transfer [the forms of adducts (B) and (C)] must induce marked rearrangement of the molecule of the adduct in comparison with that of the initial acid. In this connection the structure of the adduct

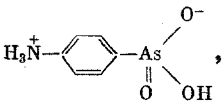
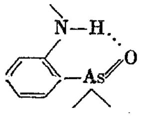
TABLE 2. Physicochemical Properties of the Compounds Obtained

Compound	Formula	Yield, %	mp, °C	Found/calculated				Empirical formula
				As	N	C	H	
(VII)	 $\mathrm{CH_2{=}CHCH_2\underset{\underset{O}{\|}}{As}(OH)_2H_2NCH_2OC_4H_3}$	88,01	105–106	$\frac{28,22}{28,47}$	$\frac{5,36}{5,32}$	$\frac{36,23}{36,51}$	$\frac{5,48}{5,37}$	$C_8H_{14}NO_4As$
(VIII)	 $\mathrm{C_6H_5CH_2\underset{\underset{O}{\|}}{As}(OH)_2H_2NCH_2OC_4H_3}$	93,38	128–129	$\frac{23,99}{23,92}$	$\frac{4,53}{4,47}$			$C_{12}H_{16}NO_3As$
(IX)		86,52	158–159	$\frac{18,79}{18,76}$	$\frac{3,74}{3,51}$	$\frac{57,08}{57,12}$	$\frac{8,67}{8,60}$	$C_{19}H_{34}NO_3As$
(X)		99,87	203 decomp.	$\frac{17,23}{16,93}$	$\frac{6,48}{6,33}$	$\frac{53,82}{54,28}$	$\frac{7,49}{7,99}$	$C_{20}H_{35}N_2O_4As$
(XI)	 $\mathrm{2\text{-}CH_3\underset{\underset{O}{\|}}{C}NHC_6H_4\underset{\underset{O}{\|}}{As}(OH)_2H_2NCH_2OC_4H_3}$	81,51	141–142	$\frac{20,85}{21,03}$	$\frac{8,52}{7,87}$	$\frac{44,39}{43,83}$	$\frac{4,82}{5,16}$	$C_{13}H_{17}N_2O_5As$

must be similar to that of the salt  Na+, the NQR frequency of which greatly differs from that of phenylarsonic acid. Therefore, marked shifts of the frequency ($\Delta\nu$) must evidently be an indication of complete proton transfer in the adduct molecule.

In NQR the specimens are investigated in the crystalline phase and the spectra are usually measured at 77°K. It is difficult to expect that under these conditions the particular adducts could exist simultaneously in different forms. The existence of adducts in the crystalline phase in a particular form is confirmed by the fact that in all the compounds investigated (except benzyl arsonate, dicyclohexylamine, and the Na salt of phenylarsonic acid) the NQR spectra consist of a single line. The two ^{75}As NQR signals in compounds (III) and (IX) evidently indicate two chemically inequivalent positions of the arsonic atom in molecules of these adducts.

With the exception of derivatives of aminophenylarsonic acids, for all the adducts investigated the deviations of the resonance frequencies from the frequencies of the initial acids have values from 6.02 to 14.32 MHz. This indicates the existence of adducts in the form of an ion pair (B) or in the form of dissociated ions (C). It is difficult to make a choice between these two forms purely on the basis of data on ^{75}As NQR spectra. We can only postulate that the maximal shifts of the resonance frequencies must correspond to the dissociated form (C).

From the small shifts of the resonance frequencies in adducts of aminophenylarsonic acids we might have inferred that these adducts have the form of H complexes (A). However, according to IR spectroscopy data, the derivatives of aminophenylarsonic acids exhibit features typical of complete or partial proton transfer [8]. The distinguishing features of the behavior of the resonance frequencies of ^{75}As NQR can evidently be explained by the fact that, according to x-ray structural analysis data [7], the initial p-aminophenylarsonic acid in the crystalline phase is a zwitterion,  , and in molecules of o-aminophenylarsonic acid and its derivatives an intramolecular H bond  is evidently present.

EXPERIMENTAL

Adduct of Benzyl Arsonic Acid and Furfurylamine (VIII). To 0.05 mole of benzyl arsonic acid (synthesized according to [9]) in 250 ml CH_3OH we added 0.06 mole (a 1.3-fold excess) of freshly distilled furfurylamine and mixed them for 45 min; the mixture was kept for 1 day, half was evaporated in vacuum and the crystals precipitated with dry ether. After drying in a vacuum desiccator above P_2O_5 the yield of furfurylamine benzyl arsonate was 13.54 g.

Using the same procedure we obtained the adducts (VII), (IX), (X), (XI) (Table 2). Adducts (I), (II), (IV), and (VI) were obtained by bubbling the gaseous amine through an alcoholic solution of arsonic acid [8].

The ^{75}As NQR spectra were measured at 77°K on an IS-3 NQR pulse spectrometer.

CONCLUSIONS

1. The authors investigate the ^{75}As NQR spectra of adducts of arsonic acids and amines.

2. They postulate complete proton transfer from the molecule of the acid to the amine in adducts of arsonic acids with amines.

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INFLUENCE OF HEAT TREATMENT OF BIMETALLIC CATALYSTS ON THE METAL SURFACE OF PLATINUM, PALLADIUM, AND RHENIUM DEPOSITED ON ALUMINUM OXIDE

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541.183:546.92:546.719

It is assumed that rhenium provides high thermal stability of aluminum–platinum–rhenium reforming catalysts, by inhibiting crystallization of platinum [1, 2]. Rhenium has also been incorporated into the composition of an Al–Pd catalyst [3].

It is difficult to reveal the actual role of rhenium in bimetallic catalysts owing to the absence of reliable methods for the separate determination of Re, Pt, and Pd. It is assumed [4] that Pt, Re/Al_2O_3 contain only individual particles of pure Re and Pt, that the overall metal surface can be determined from the amount of absorbed O_2, and that the platinum surface can be calculated from the amount of H_2 expended on the reaction with Pt/O.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of Academy of Sciences of the USSR. N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 1953-1957, September, 1981. Original article submitted January 14, 1981.

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