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Abstract

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STUDY OF THE ISOMERIZATION OF AZOXY COMPOUNDS WITH THE AID OF O^{18}

Previously ([1]), with the aid of N^{15}, we established that the conversion of azoxybenzene into *p*- and *o*-oxyazobenzenes proceeds by two different mechanisms, irrespective of the reaction conditions. In the rearrangement of azoxybenzene into *p*-oxyazobenzene, both benzene rings are hydroxylated to an equal extent:

$$\mathrm{Ph{-}\overset{+}{N}(\overset{-}{O}){=}N^{15}{-}Ph} \longrightarrow \tfrac{1}{2}\,\mathrm{Ph{-}N{=}N^{15}{-}Ph{-}OH} + \tfrac{1}{2}\,\mathrm{HO{-}Ph{-}N{=}N^{15}{-}Ph}$$

which is due to the formation of an intermediate compound of symmetrical structure. In the formation of *o*-oxyazobenzene, only the benzene ring remote from the NO group is hydroxylated and, consequently, in this case the reaction proceeds without formation of a symmetrical intermediate compound:

$$\mathrm{Ph{-}\overset{+}{N}(\overset{-}{O}){=}N^{15}{-}Ph} \longrightarrow \mathrm{Ph{-}N{=}N^{15}{-}Ph(OH)}$$

However, the data obtained with the aid of N^{15} proved insufficient for a deeper understanding of the reactions under study. In particular, a fundamentally important question remained open—whether the rearrangement proceeds inter- or intramolecularly.

In the present communication we give the results of a study of the isomerization of azoxy compounds with the aid of O^{18}. It was determined whether, in the ortho- and para-rearrangements of azoxy compounds, hydroxylation occurs at the expense of the oxygen of the azoxy group or of the oxygen of the medium, and also the influence exerted on this process by substituents (NO_2, Br, etc.). In connection with clarification of the structure of the symmetrical intermediate compound arising in the para-rearrangement, the mechanism of isomerization of one form of an azoxy compound into another (β into α) was also studied with the aid of O^{18}.

To solve these questions, azoxybenzene-O^{18}* was subjected to rearrangement in 83% sulfuric acid (at various temperatures), in chlorosulfonic acid, and under

the influence of γ-radiation. In another series of experiments, rearrangement of unlabeled azoxybenzene was carried out in a labeled medium, 83% sulfuric acid-O_4^{18} (also at various temperatures), and with

* Azoxybenzene-O^{18} was obtained by oxidation of azobenzene with 7.5% hydrogen peroxide-O^{18} (excess O^{18}—1.51 atom %); ratio of reagents 1 : 2 (cf. ([2])). The labeled hydrogen peroxide was prepared in the laboratory of A. I. Brodskii by the method developed by V. A. Lunenok. We consider it our duty to express our deep gratitude to A. I. Brodskii and V. A. Lunenok.

on heating with acetic anhydride-O_3^{18}*. The rearrangement conditions were the same as for azoxybenzene-α-N^{15} (see (1)).

In studying the question of the influence of substituents, the first objects chosen for investigation were α-p-bromoazoxybenzene, β-n'-nitroazoxybenzene, and m, m'-dinitroazoxybenzene, which were subjected to the Wallach rearrangement in labeled sulfuric acid under conditions that allowed some amount of the unreacted starting azoxy compound to be isolated. In all cases the final and unreacted starting compounds were isolated and purified under conditions analogous to those described earlier (1);

Table 1

Study of the isomerizations of azoxy compounds with the aid of O^{18}

Azoxy compound	Rearrangement conditions	Oxyazo compound obtained	O^{18} excess, at. %, in the starting azoxy compound	O^{18} excess, at. %, in the medium	O^{18} excess, at. %, in the unreacted azoxy compound	O^{18} excess, at. %, in the oxy group of the oxyazo compound
Azoxybenzene-O^{18}	HSO_3Cl; 1 h; −8°	*p*-Oxyazobenzene	1.51	0		0.01
Same	83% H_2SO_4; 8.5 days; 23°	»	1.51	0	1.49	0
» »	83% H_2SO_4; 8 min; 90°	»	1.51	0	1.54	0.1

Azoxy compound	Rearrangement conditions	Oxyazo compound obtained	O^{18} excess, at. %, in the starting azoxy compound	O^{18} excess, at. %, in the medium	O^{18} excess, at. %, in the unreacted azoxy compound	O^{18} excess, at. %, in the oxy group of the oxyazo compound
» »	83% H_2SO_4; 8 min; 150°	*o*-Oxyazobenzene-O^{18}	1.51	0		1.37
» »	UV light; 65 h; 30–40°	»	1.51	0	1.51	1.53
Azoxybenzene	83% $H_2SO_4^{18}$; 8.5 days; 23°	*p*-Oxyazobenzene-O^{18}	0	0.58	0	0.56
»	83% $H_2SO_4^{18}$; 8 min; 90°	»	0	0.58	0.01	0.59
»	83% $H_2SO_4^{18}$; 8 min; 90°	*o*-Oxyazobenzene				0.01
»	83% $H_2SO_4^{18}$; 8 min; 150°	*p*-Oxyazobenzene-O^{18}	0	0.58		0.57
»	83% $H_2SO_4^{18}$; 8 min; 150°	*o*-Oxyazobenzene				0.01
»	$(CH_3CO^{18})_2O^{18}$; 4 h; 230–240°	»	0	0.51	0	0
α-*p*-Bromoazoxybenzene	83% $H_2SO_4^{18}$; 25 min; 75°	*p*-Oxy-*n*′-bromoazobenzene-O^{18}	0	1.38	0	1.14

Azoxy compound	Rearrangement conditions	Oxyazo compound obtained	O^{18} excess, at. %, in the starting azoxy compound	O^{18} excess, at. %, in the medium	O^{18} excess, at. %, in the unreacted azoxy compound	O^{18} excess, at. %, in the oxy group of the oxyazo compound
α-*p*-Bromoazoxybenzene	83% $H_2SO_4^{18}$; 25 min; 75°	*o*-Oxy-*n*-bromoazobenzene				0.05
m,m'-Dinitroazoxybenzene	93% $H_2SO_4^{18}$; 5 min; 140°	*p*-Oxy-m,m'-dinitroazobenzene-($O^{18}H$)	0	1.78	0	1.75
β-n'-Nitroazoxybenzene	98% $H_2SO_4^{18}$; 23 h; 23°	*p*-Oxy-n'-nitroazobenzene-($O^{18}H$)	0	1.02	0*	0.96
Same	CrO_3^{18} + $CH_3CO_2^{18}H$; 15 min; 80–90°		0	1.73	0*	

* α-*p*-Nitroazoxybenzene was isolated.

o-Oxyazo compounds were additionally purified by sublimation in vacuum at 40–60°. The little-studied isomerization of one form of azoxy compounds into another was studied using as an example the conversion of β-n'-nitroazoxybenzene into α-*p*-nitroazoxybenzene. Isomerization of unlabeled β-n'-nitroazoxybenzene was carried out in a solution of chromic anhydride-O_3^{18}** in acetic acid-O_2^{18} under the conditions used by Angeli ([3]), and also under the action of 98% sulfuric acid-O_4^{18} under the conditions recently described by Gore ([4]). In the latter

* Acetic anhydride-O_3^{18} was synthesized according to the following scheme:

$$NaO^{18}H + CH_3COCl \rightarrow CH_3CO_2^{18}Na \xrightarrow{POCl_3} CH_3CO^{18}Cl \xrightarrow{CH_3CO_2^{18}Na} (CH_3CO^{18})_2O^{18},$$

** To prepare chromic anhydride-O_3^{18}, 1 part of dry CrO_3 was boiled (1 h) with 64 parts of H_2O^{18}, followed by distillation of the water.

case, along with isomerization of the β-form into the α-form, rearrangement to *p*-oxy-p'-nitroazobenzene also takes place.

In all the reactions studied, the absence of oxygen exchange between the azoxy compounds, the oxyazo compounds, and the medium was established under the conditions used. To determine the content of O^{18}, the starting and resulting compounds were subjected to pyrolysis over platinized carbon black at 900°. The carbon monoxide formed in this process was oxidized at 120° with J_2O_5 to carbon dioxide, the isotopic composition of which was analyzed mass-spectrometrically. The content of O^{18} in sulfuric acid was also determined by mass-spectrometric measurement of carbon dioxide. For this purpose, unlabeled CO_2 was shaken with water distilled from $H_2SO_4^{18}$ until the isotopic composition of the oxygen of the water and CO_2 had equilibrated.

On the basis of the results obtained (see Table 1), the following conclusions may be drawn. 1. Since it turned out that in the *para*-rearrangement the oxygen of the oxy group in all cases has the same isotopic composition as the oxygen of the medium (regardless of the conditions employed, the presence or absence of substituents, their nature, number, and position in the molecule), it follows that the hydroxyl group in the *para*-rearrangement of azoxy compounds is formed from the oxygen of the medium, i.e., the reaction is intermolecular in character. 2. In the case of the *ortho*-rearrangement, the isotopic composition of the oxygen of the oxy group of the oxyazo compound formed does not differ from the isotopic composition of the oxygen of the azoxy group of the starting azoxy compound (regardless of the reaction conditions and the presence of substituents in the molecule); consequently, in this rearrangement the oxy group of the oxyazo compounds is formed from the oxygen of the azoxy group, and the reaction is intramolecular in character. 3. Since, regardless of the isomerization conditions, the isotopic composition of the oxygen of the azoxy group of α-p'-nitroazoxybenzene does not differ from the isotopic composition of the oxygen of the azoxy group of the starting β-p'-nitroazoxybenzene, it follows that the isomerization of the β-form of azoxy compounds into the α-form proceeds intramolecularly.

The results obtained with the aid of N^{15} and O^{18} make it possible to clarify the question of the structure of the symmetrical intermediate compound arising in the *para*-rearrangement of azoxy compounds.

At present, of the four symmetrical structures (A, B, C, and D) discussed in the literature, the first three must be rejected

$$C_6H_5 - N(OH) - N(OH) - C_6H_5$$

(A)

$$C_6H_5 - N = N - C_6H_5$$

(B)

$$[\text{benzene ring}]^{+} - \text{N} = \text{N} - [\text{benzene ring}]^{+}$$

(C)

$$\text{C}_6\text{H}_5 - \text{N} - \text{N} - \text{C}_6\text{H}_5$$

$$\text{O}$$

(D)

Indeed, the N,N-diol (A), proposed earlier by Wohl ([5]), is excluded, since the hydration stage required for its formation cannot be accepted for the rearrangement carried out in chlorosulfonic acid.

The assumption that azobenzene (B) ([6]) is formed as an intermediate compound also proved untenable, since the addition of unlabeled azobenzene during the rearrangement of azoxybenzene-α-N^{15} did not cause dilution of the label in the resulting *p*-oxyazobenzene ([1]). The dication (C) is likewise unacceptable, since, according to Gore ([4]), it is formed from the unsymmetrical monocation (E)

$$[\text{benzene ring}] - \overset{+}{\text{N}}(\text{OH}) = \text{N} - [\text{benzene ring}],$$

(E)

which, as our studies ([1]) using N^{15} have shown, cannot be an intermediate compound in the Wallach rearrangement, since, regardless of the reaction conditions, complete equilibration of the isotopic composition of both nitrogen atoms of the formed *p*-oxyazo-

benzene. In addition, the dication (C) is unlikely also for energetic reasons. On the other hand, new data have now been obtained in favor of the formation of the oxide-type intermediate compound (D) proposed earlier ([1]). The intramolecular transfer of oxygen from one nitrogen atom to the other, which we observed in studying the isomerization of the β-form of azoxy compounds into the α-form, can be readily understood if it is assumed that this process proceeds through an intermediate compound in which the oxygen simultaneously belongs to both nitrogen atoms. It is quite probable that the same oxide-type intermediate compound is also formed in the para-rearrangement of azoxy compounds.*

(azoxy compound with substituents R and R') $\rightleftarrows$ (cyclic oxide-type intermediate) $\rightleftarrows$ (isomeric azoxy comp

$$\longrightarrow x\,\mathrm{HO{-}C_6H_4{-}N{=}N{-}C_6H_4{-}R'} + (1-x)\,\mathrm{R{-}C_6H_4{-}N{=}N{-}C_6H_4{-}OH}$$

Depending on the nature and position of the substituents, the formation of this intermediate compound and its subsequent transformations may proceed at different rates. The scheme given makes it possible readily to explain both the transformation of one form of an azoxy compound into another with simultaneous rearrangement into an oxyazo compound (for example, β-n'-nitroazoxybenzene is converted into α-n-nitroazoxybenzene and isomerizes into n-oxy-n'-nitroazobenzene), and the rearrangement of an azoxy compound into an oxyazo compound without simultaneous isomerization of one form into the other (for example, α-n-bromoazoxybenzene rearranges into n-oxy-n'-bromoazobenzene, but does not isomerize into β-n'-bromoazoxybenzene). In the case of unsubstituted azoxybenzene, the rate of the hydroxylation reaction of the intermediate compound greatly exceeds the rate of the reverse process—the conversion of it into the starting azoxy compound (the isotopic composition of the nitrogens of azoxybenzene-α-N^{15} isolated from the reaction unchanged is not altered ([1])).

As regards the mechanism of the ortho-rearrangement, the scheme proposed by Badger and Buttery ([7]) for a special case (rearrangement under UV irradiation) may be extended to ortho-rearrangements under the most diverse conditions.

$$\mathrm{C_6H_5{-}N(O){=}N{-}C_6H_5} \longrightarrow \mathrm{C_6H_5{-}N^{+}{-}N{=}C_6H_4(O^{-})H} \longrightarrow \mathrm{C_6H_5{-}N{=}N{-}C_6H_4OH}$$

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* This intermediate compound may be regarded both as a kinetically independent species and as a transition state.

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