DOUBLE PROTONATION OF HYDRAZO COMPOUNDS DOES NOT OCCUR IN THE REARRANGEMENT PROCESS

1960

SovietRxiv

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CHEMISTRY

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DOUBLE PROTONATION OF HYDRAZO COMPOUNDS DOES NOT OCCUR IN THE REARRANGEMENT PROCESS

(Presented by Academician B. A. Kazanskii, March 5, 1960)

Over the last 15 years a number of studies have been published on the kinetics of the rearrangement of hydrazo compounds ([1]), mainly in aqueous-alcoholic HCl solutions. On the basis of these studies it is accepted that the reaction rate in solutions of ionized acids is directly proportional to the first power of the concentration of the hydrazo compound and to the square of the concentration of hydrogen ions; in this connection the transition state is formed by a molecule of the hydrazo compound and two protons. This view is at present shared by almost all authors. The interpretation of the rearrangement mechanism set out above gives rise to objections.

Let us first turn to some experimental material from kinetic studies. The main attention has been devoted to hydrazobenzene; according to the determinations of Carlin, Nelb, and Odioso ([2]), under the action of HCl in solutions of 95% ethyl alcohol hydrazobenzene is converted into a mixture of benzidine and diphenyline in the ratio 70 : 30, which does not depend on temperature, acid concentration, or the total concentration of ions. In this connection it is accepted that the disappearing hydrazobenzene passes entirely into a mixture of benzidine and diphenyline in the ratio 70 : 30. Some authors, apparently without verification, extend this ratio also to the case of rearrangement under changed conditions, in particular in ethanol strongly diluted with water. Many of the data just cited are inaccurate.

First, the absolute amounts of diphenyline are considerably smaller than those found by Carlin, Nelb, and Odioso; moreover, the ratio of benzidine to diphenyline is closely connected with the alcohol concentration: in 95% alcohol it is 79 : 21; in 75%, 84 : 16; in 45%, 87 : 13 (in aqueous HCl solutions, 92 : 8). It is true that the ratio of benzidine to diphenyline is almost independent of the concentrations of the hydrazo compound and of the acid; however, with an increase in temperature the amount of benzidine decreases noticeably at the expense of diphenyline and other substances. Secondly, among the rearrangement products there is *o*-aminodiphenylamine (or analogous *o*-semidines), the amount of which increases with increasing alcohol concentration. Finally, rearrangement is always accompanied by an intermolecular* disproportionation reaction, which is especially noticeable with 4,4′-dimethylhydrazobenzene (and analogues with substituents in the 4- and 4,4′-positions). The amount of *p*-toluidine considerably exceeds the amount of *p*-azotoluene because alcohol also partly acts as a reducing agent for the monoprotonated hydrazo compound.

Disproportionation of hydrazo compounds and rearrangement in the cases under consideration are closely related reactions; it is completely incorrect— but, however, to consider, as Carlin and Uytz do (4), that the action of a proton is required for the disproportionation of a monoprotonated hydrazo compound.

The results of the rearrangement of hydrazobenzene (I) and analogs are given in Table 1. In a series of experiments, a solution of hydrazobenzene (0.01 mole) in alcohol, rapidly cooled under nitrogen, is immediately mixed with a solution of HCl (0.1 mole), total volume 100 ml; the mixture is kept for 2 hours at 0°C, the crystals of benzidine hydrochloride are separated and converted into the sulfate; the alcohol is evaporated at 10—20°, the residue is diluted with water, the basic portion of the acid is

Table 1

Experiment no.	Hydrazo compound	Alcohol concentration, %	Benzidines, %	Diphenylines, %	*o*-semidines, %	Anilines, %	Azo compounds, %	Sum of all substances, %
1	I	99.9	75.5	19.0	2.3	1.3	1.3	99.4
2	I	95.0	72.7	19.6	2.0	2.1	2.2	98.6
3	I	95.0	73.0	19.4	2.2	2.3	2.4	99.3
4	I	95.0	56.5	23.8	2.6	8.1	8.0	99.0
5	I	85.0	79.0	16.9	1.4	1.1	1.1	99.5
6	I	75.0	81.2	15.2	1.0	1.1	1.1	99.6
7	I	75.0	80.5	15.4	1.2	1.1	1.1	99.3
8	I	60.0	83.2	13.5	0.9	0.9	0.9	99.4
9	I	45.0	84.3	12.6	0.7	0.9	1.0	99.5
10	I	–	89.8	7.7	0.2	0.9	0.9	99.5
11	II	95.0	87.0	10.9	0.7	0.5	0.5	99.6
12	III	95.0	–	–	58.1	23.0	16.1	97.2
13	IV	99.9	65.7	16.9	2.6	4.7	4.5	94.4

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* Let us recall (3) that if an equimolecular amount of 2,2′-dimethoxyhydrazobenzene is added to hydrazobenzene hydrochloride (0.01 mole) in ether at 0°C, then after the mixture has stood for 24 hours neither aniline nor benzidine is detected. Along with partially regenerated hydrazobenzene and the rearrangement products of 2,2′-dimethoxyhydrazobenzene, the following are found: 2,2′-dimethoxyazobenzene (0.130 g), azobenzene (0.526 g), and *o*-anisidine (0.787 g).

Experiment no.	Hydrazo compound	Alcohol concentration, %	Benzidines, %	Diphenylines, %	*o*-semidines, %	Anilines, %	Azo compounds, %	Sum of all substances, %

carefully neutralized, and *o*-semidine and azobenzene are extracted with ether (5). In the aqueous part remains benzidine, diphenyline, and aniline. Benzidine sulfate is reprecipitated; the sum of diphenyline and aniline is determined by diazotization, and the amount of aniline is determined after repeated distillation with steam.

In experiment 4 (I) is added over 15 min to the acid solution at 45—50°. In experiments 2 and 7 the reagent concentrations are reduced: hydrazobenzene (0.01 mole) is added uniformly over 4 hours to a solution of HCl (0.04 mole) in alcohol (200 ml) at 0°C and left to stand for 16 hours. In experiment 10, (I) in a benzene–toluene solution is shaken with an aqueous solution of HCl (0.1 mole in 60 ml) at 0°C.

2,2′-Dimethylhydrazobenzene (II), 4,4′-dimethylhydrazobenzene (III), and 2,2′-dimethoxyhydrazobenzene (IV) are added uniformly over half an hour to a solution of HCl (0.1 mole) in alcohol (100 ml) at 0°C. Treatment of the mixtures is similar to that described for (I), see also (5).

The results of the rearrangement of (IV) are fundamentally at variance with the data of Ingold and Kidd (6), who did not detect substances isomeric with *o*-dianisidine. Let us add that the base of dianisidine, obtained by the action of ammonia on the hydrochloride precipitate, melts at 133—135° (but not at 138°!) and contains about 4% impurities, predominantly isomeric diphenyline, separable by special purification (5).

As regards the interpretation of the results of kinetic studies, we shall refer to the article by Benton, Ingold, and Mala (7). The authors note that the kinetic order of the reaction with respect to hydrogen ions in the case of hydrazobenzene is 1.85; for 2,2′-dimethyl- and 3,3′-dimethylhydrazobenzene, respectively, 1.6 and 2.0. Carlin and Odioso (8) explain the deviations from the desired figure 2 by the circumstance that during the reaction a significant part of the hydrazo compound is in a bound state with the acid molecule. Benton, Ingold, and Mala, on this same point, ask the question whether, in determining the kinetic order of the reaction, one should not have

in view not of the acid concentration, but of Hammett' s function?* Blackadder and Hinshelwood (9), taking as their example 2,2′-dimethylhydrazobenzene, consider that some monoprotonated hydrazo compounds rearrange in part spontaneously.

It seems to us, on the basis of recent investigations, that the questions just touched upon should be answered differently. It has been shown (10) that hydrazobenzene and its closest analogues, when heated (110°) with amine hydrochlorides (and sometimes with small amounts of weak acids), rapidly disproportionate, while the amounts of rearrangement products are, as a rule, insignificant. Evidently, traces of HCl combine with the hydrazo compound, after which the reaction proceeds:

$$2\,(\mathrm{RNH}-\overset{+}{\mathrm{N}}\mathrm{H_2R})\,\overline{\mathrm{Cl}} \rightarrow \mathrm{RN{::}NR} + 2\,\mathrm{RNH_3Cl}. \tag{1}$$

Thus, irrespective of the structure of the hydrazo compound, its monoprotonated molecule acquires the ability to be very readily reduced and oxidized, but it is not possible to detect an ability to rearrange spontaneously, as Blackadder and Hinshelwood suppose. Moreover, as will be seen, such an assumption is quite unnecessary.

Further, certain conclusions suggest themselves on considering the stability of salts of hydrazo compounds under the conditions of their preparation (5). It has been established that hydrazobenzene and its analogues with substituents in the 2-, 3-, and 3,3′-positions form relatively stable salts (which rearrange comparatively slowly under the conditions of their preparation), owing to which they can sometimes be isolated in very good yields. By contrast, hydrazo compounds with substituents in the 2,2′- and 4,4′-positions do not form stable salts. In addition, cases are not rare in which salts of more basic hydrazo compounds (in particular, hydrazobenzene hydrochloride) rearrange considerably more slowly than salts of less basic hydrazo compounds.

Taking this into account, it becomes evident that if hydrazo compounds forming relatively stable salts can, in their relation to acids, to some extent be likened to dibasic bases of the usual type, then in the remaining cases the difference between the rates of monoprotonation and of the subsequent rearrangement may be so small that the kinetic order of the rearrangement reaction with respect to hydrogen ions, even if it approaches the desired figure 2, does so only by chance.

Turning to the question of how probable double protonation of hydrazo compounds is for the occurrence of rearrangement, we note first of all that the unreality of "hydrazobenzene dihydroiodide" (12) (as well as of "hydrazobenzene dihydrochloride" (3)), which serves as a support for some authors (13), was proved already quite a long time ago (11). Recently we have become convinced that, even in a series of considerably more basic hydrazines—aliphatic-aromatic ones—it is not possible to obtain appreciable amounts of diacid salts even under very severe conditions; for example, by treating *N*-methyl-*N*′-phenylhydrazine (0.001 mole) in a benzene-toluene solution (20 ml) with hydrogen bromide (0.004 mole) at 0°. Under exactly the same conditions, 2,2′-dichlorohydrazobenzene—a base considerably weaker than pentachloroaniline—rearranges elusive rapidly (see also (5)). It is evident that so great a rearrangement rate cannot be ascribed to negligible traces of a diprotonated hydrazo compound, since only such amounts of the latter could be involved in the example considered.

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* An acidity function characterizing the tendency of the medium to transfer a proton to a neutral base.

Let us note the following facts as well. There exist hydrazo compounds, for example 2,2′-dimethoxyhydrazobenzene, which react immediately and vigorously when added in small portions, indifferently, to 85% or glacial acetic acid at 20°. On the other hand, for example, 3,3′-dichlorohydrazobenzene is incapable of rearranging even on heating (110°) with the indicated acid: as a result of half an hour of heating, only about 2.5% of the hydrazo compound disproportionates. Thus, even single protonation[1] of 3,3′-dichlorohydrazobenzene in acetic acid proceeds with difficulty. If one takes into account that the difference in basicity between the initial and monoprotonated hydrazo compounds is very large, whereas 3,3′-dichloro- and 2,2′-dimethoxyhydrazobenzene do not differ so very strongly in basicity (the difference in their corresponding pK values apparently does not exceed 2–2.5 units[2]), the groundlessness of requiring double protonation of 2,2′-dimethoxyhydrazobenzene under the conditions indicated above becomes evident.

In view of all that has been set forth, in studying rearrangement in media of nonionized acids we have adopted a mechanism based on intermolecular interaction of the monoprotonated hydrazo compound and the acid, representing the transition state as follows:

$$(\mathrm{RNH}-\overset{+}{\mathrm{N}}\mathrm{H_2R})\,\overset{-}{\mathrm{X}}\ldots\mathrm{HX}. \tag{2}$$

In cases of ionized acids, the interesting proposal of Blackadder and Hinshelwood deserves attention; they consider that the monoprotonated hydrazo compound rearranges already upon approach of a proton. For aqueous and aqueous-alcoholic solutions we shall have:

$$\mathrm{RNH}-\overset{+}{\mathrm{N}}\mathrm{H_2R}\ \mathrm{H_3}\overset{+}{\mathrm{O}}. \tag{3}$$

In absolute alcohol, or in alcohol close to it in concentration, the catalyst of the reaction is the ethoxonium ion; it is significant that although the reaction rate in 99.9% alcohol is approximately 150 times greater than in 95%, the results of the rearrangement of hydrazobenzene are almost identical (cf. expts. 1 and 3).

The present work was carried out jointly with L. G. Krolik.

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[1] V. O. Lukashevich, L. G. Krolik, DAN, **120**, No. 2, 316 (1958).

[2] V. O. Lukashevich, L. G. Krolik, DAN, **129**, No. 1, 117 (1959).

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