Disproportionation of Hydrazo Compounds on Heating with Salts of Amines and Weak Acids

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V. O. Lukashevich and L. G. Krolik

Disproportionation of Hydrazo Compounds on Heating with Salts of Amines and Weak Acids

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It is well known that hydrazo compounds of the benzene series, upon moderate heating (100–150°) in an inert medium, slowly decompose with the formation almost exclusively of disproportionation products*. According to our determinations, if an equimolecular amount of azobenzene is added to hydrazobenzene in order to keep it in the molten state, and this mixture is heated at 110°, then after 60 min., judging from the amount of aniline formed, the disproportionation of hydrazobenzene amounts to about 7% of theory. The decomposition of 2,2′-dimethylhydrazobenzene in the presence of an equimolecular amount of the corresponding azo compound proceeds much more slowly. Almost as rapidly as hydrazobenzene, the isomeric 3,3′- and 4,4′-dimethylhydrazobenzenes decompose (ligroin was added to the latter substance). The disproportionation of these hydrazo compounds is expressed, respectively, by the figures: 1; 4.8, and 10.4% of theory (see Table 1).

We have now established that in the presence of hydrochloride salts of amino compounds the disproportionation of hydrazo compounds is sharply accelerated. Thus, for example, when a finely ground mixture of equimolecular amounts of hydrazobenzene and aniline hydrochloride is heated (110°), the mass, rapidly turning red, passes into the molten state, and after only 15 min. the disproportionation of hydrazobenzene reaches 80%; the reaction mixture has a bright reddish coloration, and among the rearrangement products only traces of *o*-aminodiphenylamine can be detected.

If the amount of aniline hydrochloride is reduced to 10% of the molar amount, the decomposition of hydrazobenzene proceeds more slowly, but nevertheless after one hour of heating it amounts to somewhat more than 80% (experiment No. 2 in Table 1). With stronger heating (140–160°) the partially resinified mass contains considerably larger amounts of rearrangement products, among them also benzidine (about 2%).

The action on hydrazobenzene of benzidine dihydrochloride and aniline hydrochloride is almost the same, but benzidine monohydrochloride acts considerably more weakly (experiment No. 5 in Table 1), which is explained by the weaker dissociation of this salt, associated with the greater basicity of benzidine. Taking advantage of the fact that benzidine, aniline, and benzidine hydrochloride constitute a series of compounds of successively decreasing basicity, we were able to obtain the relatively difficultly accessible benzidine monohydrochlorides and analogs by the action of aniline on the dihydrochlorides of these bases in aqueous solutions; the yields exceed 85–90% of theory.

The mechanism of the reaction described is as follows: very small amounts of HCl, due to the weak dissociation of hydrochloride

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* In the naphthalene series, as we have shown, rearrangement occurs under analogous conditions (1).

Table 1

Experiment No.	Starting substances: hydrazo compound (0.005 mole)	Starting substances: amine salt or acid (0.0005 mole)	Obtained: monoamine, %	Obtained: azo compound, %	Recovery of hydrazo compound, %	Sum of all substances, %
1	Hydrazobenzene	–	3.5	–	–	–
2	Hydrazobenzene	Aniline hydrochloride	40.7	42.0	13.0	95.7
3	Hydrazobenzene	Aniline sulfate	3.5	–	–	–
4	Hydrazobenzene	Benzidine dihydrochloride (0.00025 mole)	39.6	40.8	17.0	97.4
5	Hydrazobenzene	Benzidine monohydrochloride	28.0	27.7	39.7	95.4
6	Hydrazobenzene	Benzoic acid	25.2	25.1	46.4	96.7
7	Hydrazobenzene	Acetic acid	17.0	18.2	61.3	96.5

Experiment No.	Starting substances: hydrazo compound (0.005 mole)	Starting substances: amine salt or acid (0.0005 mole)	Obtained: monoamine, %	Obtained: azo compound, %	Recovery of hydrazo compound, %	Sum of all substances, %
8	Hydrazobenzene	Butyric acid	14.5	15.0	68.1	97.6
9	2,2′-Dichlorohydrazobenzene	Aniline hydrochloride	0.5	0.8	94.8	96.1
10	3,3′-Dichlorohydrazobenzene	–	1.0	1.1	–	–
11	3,3′-Dichlorohydrazobenzene	Aniline hydrochloride	31.3	33.0	32.2	96.5
12	4,4′-Dichlorohydrazobenzene	–	2.0	3.0	–	–
13	4,4′-Dichlorohydrazobenzene	Aniline hydrochloride	46.7	47.2	2.0	95.9
14	2,2′-Dimethylhydrazobenzene	–	0.5	–	–	–
15	2,2′-Dimethylhydrazobenzene	*o*-Toluidine hydrochloride	34.0	35.0	27.4	96.4
16	3,3′-Dimethylhydrazobenzene	–	2.4	–	–	–
17	3,3′-Dimethylhydrazobenzene	Aniline hydrochloride	41.1	42.8	12.1	96.0
18	4,4′-Dimethylhydrazobenzene	–	5.2	5.6	–	–

Experiment No.	Starting substances: hydrazo compound (0.005 mole)	Starting substances: amine salt or acid (0.0005 mole)	Obtained: monoamine, %	Obtained: azo compound, %	Recovery of hydrazo compound, %	Sum of all substances, %
19	4,4′-Dimethylhydrazobenzene	Aniline hydrochloride	46.5	48.7	Traces	95.2
20	2,2′-Dimethoxyhydrazobenzene	–	14.5	15.5	–	–
21	2,2′-Dimethoxyhydrazobenzene	*o*-Anisidine hydrochloride	39.0	40.5	7.5	87.0

of salts of amino compounds under moderate heating are captured by the hydrazo compound, which leads to the formation of the corresponding hydrochloride:

$$\mathrm{RNH-NHR+HClleftarrows|RNH-\overset{+}{N}H_2R|\overline{Cl}},\tag{1}$$

which is subject to dissociation to a greater extent than the original hydrochloride salts of amino compounds. Using hydrazobenzene hydrochloride as an example, we showed (2) that this substance, when in an atmosphere of inert gas, already at ordinary temperature undergoes an oxidation–reduction transformation, as a result of which azobenzene and aniline are obtained; upon moderate heating this process is sharply accelerated:

$$\mathrm{2|RNH-\overset{+}{N}H_2|\overline{Cl}\rightarrow RN=NR+2|RN\overset{+}{H}_3|\overline{Cl}}.\tag{2}$$

Reactions (1) and (2) explain the formation of the products of hydrazobenzene disproportionation under the conditions of interest to us.

We think, moreover, that the interaction of hydrazobenzene hydrochloride with HCl:

$$\mathrm{|RNH-\overset{+}{N}H_2R|\overline{Cl}+HCl}\rightarrow \text{rearrangement substances},\tag{3}$$

would inevitably have led to rearrangement products. However, upon accumulation in the reaction mixture of a very large excess of the hydrazo compound during almost the entire course of the process under consideration, the formation of significant amounts of rearrangement products could occur only at the very end, at the moment when the hydrazo compound had been exhausted. In confirmation of what has just been said, it may be added that, according to experimental data, the rate of formation of monohydrochloride

hydrazobenzene (1) is considerably greater than the rate of the subsequent rearrangement. Indeed, according to our data (^{2}), hydrazobenzene hydrochloride is obtained almost quantitatively when HCl in ether solution is added gradually to an equimolecular amount of hydrazobenzene in the same ether solution.

If the individual characteristics of other hydrazo compounds are taken into account, it may be considered that, in general, they follow the example of hydrazobenzene (see Table 1).

Similar results are obtained in the cases of 2,2′- and 3,3′-dimethylhydrazobenzenes (experiments Nos. 15 and 17, Table 1). The more acid-sensitive 4,4′-dimethylhydrazobenzene is destroyed more rapidly (experiment No. 19), and especially 2,2′-dimethoxyhydrazobenzene. Disproportionation of the latter compound proceeds comparatively rapidly even in the absence of salts; when *o*-anisidine hydrochloride is added, the reaction mixture partially resinifies, and, in addition to the disproportionation products, dianisidine is formed (experiment No. 21). The behavior of dichlorohydrazobenzenes deserves attention: the 2,2′-isomer, which reacts with acids with the greatest difficulty, remains almost unchanged (experiment No. 9); on the contrary, 4,4′-dichlorohydrazobenzene, which under ordinary conditions is much less sensitive to acids than, for example, hydrazobenzene, is destroyed almost completely (experiment No. 13). Evidently, in the first case equilibrium (1) is shifted very strongly to the left, so that the formation of 2,2′-dichlorohydrazobenzene hydrochloride practically does not take place under the conditions considered; in the second case, the completeness of destruction of the 4,4′-dichlorohydrazo compound is explained by the high rate of the oxidation-reduction transformation of the hydrazo-compound hydrochloride that is formed (see equation (2)), which is apparently characteristic of all hydrazo compounds with substituents in the para position in the hydrazo group.

Disproportionation of hydrazo compounds is also catalyzed by weak acids. The action on hydrazobenzene of benzoic acid (^{3}) (K_{diss} at 25° $= 6.5 \cdot 10^{-5}$), acetic acid (^{4}) (K_{diss} at 25° $= 1.845 \cdot 10^{-5}$), and butyric acid (^{5}) (K_{diss} at 25° $= 1.55 \cdot 10^{-5}$) was tested in amounts of 0.1 mole relative to hydrazobenzene. It should be noted that at normal temperature the conversion of hydrazobenzene dissolved in glacial acetic acid is complete only after several days; anhydrous butyric acid acts much more slowly. As was to be expected, disproportion—

Table 2

Experiment No.	Starting substances: hydrazo compound (0.01 mole)	Starting substances: acid (15 ml)	Temperature, °C	Duration of experiment	Obtained: monoamines, %	Obtained: azo compounds, %	Obtained: compounds not reducing, %	Sum of all substances, %
1	Hydrazobenzene	98% acetic	18–20	10 days	14.0	15.6	60.5	90.1
2	4,4′-Dichlorohydrazobenzene	35% hydrochloric	5–10	30 min.*	17.0	20.1	58.2	95.3
3	2,2′-Dimethylhydrazobenzene	98% acetic	18–20	10 days	6.2	6.4	76.0	88.6
4	4,4′-Dimethylhydrazobenzene	98% acetic	18–20	1 day	33.5	34.6	19.9	88.0
5	2,2′-Dimethoxyhydrazobenzene	100% butyric	2–20	1 day	25.0	26.2	35.0	86.2
6	4-Ethoxyhydrazobenzene	98% acetic	18–20	1 day	26.0	27.4	Not determined	—

* The substance is dissolved in 15 ml of benzene and shaken with the acid.

ation proceeds most deeply in the presence of benzoic acid (50.4%); next come acetic (34%) and butyric (29%) acids.

There can hardly be any doubt that in these cases as well the process proceeds in two stages: the monoprotonated hydrazo compound formed, before it has time to rearrange under the influence of the weak acid, undergoes an oxidation-reduction transformation according to equation (2).

In connection with what has just been said, we wish to show how extensive the disproportionation of certain hydrazo compounds is in the course of rearrangement; this applies especially to compounds with substituents in the para position to the hydrazo group, many of which readily react with weak acids (see Table 2). The disproportionation of 4,4′-dichlorohydrazobenzene amounts to 34% even when working with concentrated hydrochloric acid (cf. (6)); upon dilution of the acid it increases sharply.

Experimental Part

Disproportionation of hydrazo compounds on heating. The reagents (see Table 1) in a test tube under nitrogen are immersed in a glycerin bath heated to 111-112° and left in it for 60 min, after which the test tube is rapidly cooled and the contents are extracted with benzene, to which a little ether has been added.

Subsequent operations are as follows. In experiments with hydrazobenzene and the three isomeric hydrazotoluenes, the benzene-ether solution is cooled with ice and shaken vigorously for several seconds with a large excess of a similarly cooled 1% hydrochloric acid solution. After separation from the benzene layer, the acidic solution is made alkaline and boiled; the amount of aniline or toluidine distilled over with the steam is determined by the usual diazotization; qualitatively, these amines are identified after conversion into benzoyl derivatives. The first drops of nitrite cause the appearance of a violet-red coloration of the diazo solution, which indicates the presence of traces of *o*-semidine, volatile with steam. The benzene-ether solution, again cooled with ice, is shaken vigorously for 10-15 min with 12-15% hydrochloric acid (5-8 ml), diluted with water to dissolve the precipitate that has separated, and the total amount of rearrangement products is determined by diazotization. The azo compound remains in the benzene-ether solution; after evaporation of the solvent it is easy to verify that this is an almost pure substance. In experiments with the three isomeric dichlorohydrazobenzenes, hydrochloric acid in the form of a 4-5% solution is used to extract the corresponding chloroanilines; for the rearrangement, a 30% hydrochloric acid solution is used. In the experiment with 2,2′-dichlorohydrazobenzene, small amounts of the azo compound formed were determined colorimetrically (7). The principal amounts of azo compounds, which are poorly soluble in organic solvents—these include 4,4′-dichloroazobenzene, 2,2′-dimethoxyazobenzene, and in part 4,4′-dimethylazobenzene—are best isolated directly from the reaction mass; the separated crystals of the azo compound are thoroughly washed with strongly diluted hydrochloric acid. In experiment No. 21 with 2,2′-dimethoxyhydrazobenzene, no hydrazo compound is present in the reaction products; instead, Table 1 gives the amount of rearrangement products.

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