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Abstract

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ON THE MECHANISM OF THE REARRANGEMENT OF HYDRAZO COMPOUNDS

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Until recently almost all investigators accepted that, in ionized acids, the rate of rearrangement of hydrazo compounds is directly proportional to the first power of the concentration of the hydrazo compound and to the square of the concentration of hydrogen ions (1). In an article (2) we showed the untenability of this hypothesis. Its proponents, however, in connection with the broadening of the range of hydrazo compounds studied, have begun to revise the basic propositions of the hypothesis. Thus, according to the data of White and Preisman (3), for N-methylhydrazobenzene in aqueous methanol the order of the reaction with respect to acid varies from 1.00 to 1.88, increasing with increasing concentration of the HCl used. According to Ingold, Hughes, and Benthrop (4), for 1,1- and 1,2-hydrazonaphthalenes the kinetic order with respect to acid is equal or close to 1.0; for 2,2-hydrazonaphthalene and some mixed benzeno-naphthalene compounds the order numbers are fractional; in some cases they approach 2.0 as the acidity of the medium increases. According to the authors, in addition to the known (above-mentioned) kinetic dependence, there also exists a linear dependence, established by them for the first time* (!):

$$\text{rate of rearrangement} \propto (\text{hydrazo})(H^+). \qquad \text{(I)}$$

Where the kinetic order with respect to acid is expressed by fractional numbers, they concur with Blackadder and Hinshelwood (7), who believe that a monoprotonated hydrazo compound (*o*-hydrazotoluene) partially rearranges spontaneously.

Ignoring certain important properties of monoprotonated hydrazo compounds (see below), investigators of the kinetics of rearrangement state categorically that if the kinetic order with respect to acid is 2.0, then the hydrazo compound adds two protons, without considering the possibility of another mode of action of the acid on the monoprotonated molecule.

At one time it was firmly shown that the diacid salts described in the literature – “diiodohydrate of hydrazobenzene” of Pongratz (8) and the dihydrochloride of hydrazobenzene, Orelkin’ s “green salt” (9)—arose as a result of experimental errors (10); therefore later references by Hammond and Carlin (11,12) to these salts cause only bewilderment. Furthermore, we showed (13) that the formation of appreciable amounts of diacid salts in a series of fatty-aromatic hydrazines, even with strong acids, is excluded. Naturally, there can be no question that rearrangement requires double protonation of substances considerably weaker in basicity—hydrazo compounds—many of which rearrange very rapidly in weak acids, for example in acetic acid under ordinary conditions (see Table 1).

In the presence of acids the rearrangement is invariably stepwise: the monoprotonated molecule that has formed rearranges only under the condition of further action of the acid. The most

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[*] It cannot be left unmentioned that a similar proposition was developed by Ingold 30 years ago (5), but in 1950 (6) the author abandoned it.

Table 1

Experiment no.	Hydrazo compound	M.p. of hydrazo, °C	Yield of hydrazo salt, % of theory	Duration of reaction with acid, 20° C	Amount of hydrazo that disappeared, % of theory
1	Hydrazobenzene	–	92	3 h	50.5
2	2-Chlorohydrazobenzene	71	66	26 h	43.3
3	3-Chlorohydrazobenzene	58–59	88	146 h	53.1
4	4-Chlorohydrazobenzene	90–91	13	26 h	64.0
5	2,2′-Dichlorohydrazobenzene	–	–	720 h	0
6	3,3′-Dichlorohydrazobenzene	–	54	720 h	0
7	4,4′-Dichlorohydrazobenzene	–	–	120 h	63.0
8	2-Methylhydrazobenzene	102–103	13	1 h	51.0
9	3-Methylhydrazobenzene	–	90	1 h	54.0
10	4-Methylhydrazobenzene	91	22 (70)	8 min	57.4
11	2,2′-Dimethylhydrazobenzene	–	10	20 min	39.0
12	3,3′-Dimethylhydrazobenzene	37–38	90	8 min	47.4

Experiment no.	Hydrazo compound	M.p. of hydrazo, °C	Yield of hydrazo salt, % of theory	Duration of reaction with acid, 20° C	Amount of hydrazo that disappeared, % of theory
13	4,4′-Dimethylhydrazobenzene	–	–	10 min	33.0
14	2-Methoxyhydrazobenzene	83–84	–	30 sec	50.0
15	4-Methoxyhydrazobenzene	–	–	10 sec	85.0*
16	2,2′-Dimethoxyhydrazobenzene	–	10	30 sec	53.6
17	3,3′-Dimethoxyhydrazobenzene	67–68	51.6	8 min	32.0
18	4,4′-Dimethoxyhydrazobenzene	127–128	–	2 sec	100.0
19	2,2′-Diethoxyhydrazobenzene	–	63 (90)	10 sec	40.0
20	3,3′-Diethoxyhydrazobenzene	89–90	29	10 min	40.0
21	4,4′-Diethoxyhydrazobenzene	117–118	–	2 sec	100.0
22	1,1′-Hydrazonaphthalene	147–148	(70–75)	10 sec	40.8
23	1,2′-Hydrazonaphthalene	154–155	(70–75)	30 sec	35.1
24	2,2′-Hydrazonaphthalene	135–136	(70–75)	60 sec	41.8

* It is clear that this experiment gives only a very approximate value for the reaction rate.

This mechanism is evident for the process in the presence of nonionized acids (II):

$$(\mathrm{RNH}-\overset{+}{\mathrm{N}}\mathrm{H_2R})\,\mathrm{X}+\mathrm{HX}\rightleftarrows(\mathrm{RNH}-\overset{+}{\mathrm{N}}\mathrm{H_2R})\,\mathrm{X}\ldots\mathrm{HX}\rightarrow\text{rearrangement products,}\qquad\text{(II)}$$

where the transition state is due to the intermolecular interaction of the monoprotonated hydrazo compound and the acid (^{13}).

While disagreeing with Blackadder and Hinshelwood’ s hypothesis concerning the partial spontaneous rearrangement of monoprotonated hydrazo compounds, we consider their suggestion expedient that in ionized acids a monoprotonated hydrazo compound rearranges already upon approach of the proton (^{7}). In weak acids the catalyst of this reaction is, apparently, mainly the nonionized acid molecule.

It may be asserted that hydrazo compounds are completely unsuitable for any valuable kinetic studies, since they only in a purely formal sense resemble dibasic bases of the usual type; and if the rate of monoprotonation depends on the basicity of the initial hydrazo compound, then the rate of the subsequent stage is practically unrelated to the basicity of the monoprotonated molecule, but is determined by another of its properties—stability in the presence of an acidic agent. If the difference in the rates of the first and second phases is considerable, the illusion of diprotonation is created, which may occur for those compounds that are capable of forming salts comparatively resistant to further action of the acid (hydrazobenzene, 2-, 3-chloro-, 3,3′-dichloro-, 3-methyl-, 3,3′-dimethylhydrazobenzene; see Table 1). In a number of cases, however (see experiments nos. 15, 16, 18, 19, 21, 22, 23, 24), monoprotonated hydrazo compounds are very unstable toward acids; in other words, the rate of the second phase here is very high, and only this simple fact, which becomes obvious on the basis of familiarity with the salts of hydrazo compounds, is confirmed by their equations by kinetic investigators, convinced that, on the basis of similar examples—

they prove the existence of a "spontaneous" rearrangement of monoprotonated hydrazo compounds.

It must be noted that spontaneous rearrangement is also in contradiction with other facts. Let us turn to the reaction, established by us, of disproportionation of hydrazo compounds on heating (100–110°) in the presence of traces of HCl or weak acids $^{(14)}$. The presence of spontaneous rearrangement would undoubtedly have manifested itself in the fact that, along with the disproportionation products, rearrangement products would have appeared in appreciable amounts; this, as a rule, does not occur, and in particular in the important case of *o*-hydrazotoluene (see above).

Compounds that are especially unsuccessful for elucidating the true nature of the rearrangement are the hydrazonaphthalenes. Because of the extreme instability of the monoprotonated hydrazo compounds (fine dispersion of salts in a heterogeneous medium; see below), the difference in the rates of the first and second phases is insignificant, separation of the rearrangement into stages is very difficult, and the whole process as a whole proceeds, understandably, very rapidly. Thus, for example, in a mixture of 95% acetic acid and dioxane at 20°, after 10 sec about 41% of 1,1′-hydrazonaphthalene is rearranged; after 30 sec, 35% of the 1,2′-isomer; and after 60 sec, 41.8% of the 2,2′-isomer. Contrary to the data of Banthorp, Hughes, and Ingold, it is possible to detect the salts of the named hydrazonaphthalenes: 0.002 mole of the hydrazo compound is dissolved in dioxane (8 ml), diluted with ether (40 ml), and at −8—−10° 1 mole of HCl in ether (15 ml) is immediately introduced. An abundant, very finely dispersed precipitate of the hydrochloride of the hydrazo compound at once separates, which cannot be isolated. However, if immediately after precipitation of the hydrochloride the whole mixture is alkalized, then on oxidation with mercuric oxide about 70–75% of the initial hydrazo compounds is regenerated in the form of azo compounds (these numbers in Table 1 are given in parentheses). We add that by visual estimation it is not difficult to be convinced that the precipitates of the hydrochlorides of the corresponding diamines (calculated amounts) are small here.

It is expedient to contrast 2,2′-diethoxyhydrazobenzene (experiment No. 19) and, respectively, 2,2′-dimethoxyhydrazobenzene (experiment No. 16) with the 1,1- and 1,2-hydrazonaphthalenes; the rates of rearrangement of these are close to those for the aforementioned hydrazonaphthalenes, and there can hardly be any doubt that the "kinetic order with respect to acid"will not differ substantially here from 1.0. But in the example of 2,2′-diethoxyhydrazobenzene, the two-phase character of the rearrangement is clearly visible: the hydrochloride of the hydrazo compound, evidently because of the coarse-grained nature of the precipitate (in ether), can be isolated in an amount of 60–65% of theory; if, however, the whole mixture is alkalized immediately after precipitation of the hydrochloride and then oxidized with mercuric oxide, about 90% of the initial hydrazo compound is regenerated in the form of the azo compound (in the table this figure is given in parentheses). It is curious that the amount of isolated hydrochloride of 2,2′-dimethoxyhydrazobenzene does not exceed 10% of theory.

Of great interest are 4,4′-dimethoxy- and 4,4′-diethoxyhydrazobenzene (experiments Nos. 18 and 21), whose rates of transformation in acids are especially high: after 2 sec the hydrazo compound completely disappears, with about 80% of disproportionation products being formed; the maximum amounts of *o*-semidines, isolable under special conditions, do not exceed 10% of theory. It is clear that here there is no possibility of detecting intermediates, and nevertheless these examples impeccably prove the stepwise character of the entire process: as has been repeatedly stated (2,13,14), the disproportionation products are the result of a secondary reaction—the interaction of two molecules of a monoprotonated hydrazo compound (III):

$$2(\mathrm{RNH}-\overset{+}{\mathrm{N}}\mathrm{H_2R})\,\mathrm{X^-} \rightarrow \mathrm{RN}=\mathrm{NR}+2\mathrm{R}\overset{+}{\mathrm{N}}\mathrm{H_3X^-}. \qquad \text{(III)}$$

The values given (80 and 10%) testify, in addition, that the rate of the bimolecular reaction (III) considerably exceeds the rate of transformation of the monoprotonated hydrazo compound into an *o*-semidine.

Experimental Part

Table 1 gives the melting points of less well studied compounds. As can be seen, Croce and Gettler[15] in a number of cases did not have pure substances; the yields of the hydrazo-compound hydrochlorides, obtained as usual in ether at

−8 to −10°, are also indicated there. In experiments Nos. 2, 3, and 6, instead of 1 mole, 2 moles of HCl were taken per 1 mole of hydrazo compound, and nevertheless in experiment No. 2, 30% remains in solution, and in experiment No. 6, 41.5% of the starting hydrazo compounds. If the hydrochlorides are of low stability, then the precipitated deposits must of course be filtered and alkalized as rapidly as possible. In cases of 4,4′-substituted hydrazobenzenes, as well as in experiments Nos. 5 and 15, no salt can be detected.

In experiments Nos. 13, 16, 18, 19, 21, 22, 23, and 24, 0.002 mole of hydrazo compound was dissolved in 8 ml of dioxane, 20 ml of 95% acetic acid was immediately introduced, and after exactly the indicated time the mixture was neutralized with a solution of NaOH in aqueous methanol cooled to −5°, oxidized with mercuric oxide at 20-25°, and filtered after 20–30 min. To extract the azo compound, the precipitate on the filter was repeatedly washed with large amounts of heated benzene, then with ether, shaken with water to remove the alcohol and dioxane, and the amino compounds were extracted with hydrochloric acid. On evaporating the organic solvent, the azo compound was obtained; when necessary it was purified by boiling with a saturated solution, at 5–7°, of the same azo compound in 90% ethanol. To obtain the final values for the disappeared hydrazo compounds, it is necessary to take into account the azo compounds formed as a result of disproportionation. Their amounts usually correspond to the amount of anilines determined by steam distillation from the alkalized hydrochloric-acid solutions. In an experiment with hydrazobenzene (not included in Table 1), where 8 ml of dioxane and 20 ml of acid were taken per 0.002 mole of hydrazo compound, after 800 h 68% of the starting hydrazo compound had disappeared. In an analogous experiment with *o*-hydrazotoluene, after 24 h 62% had disappeared.

All other experiments were carried out without dioxane. In experiment No. 15 the hydrazo compound was dissolved in 1.5 ml of ether; in experiments Nos. 1, 2, 4, 10, 11, 12, 15, 17, and 20, 20 ml of acid were taken; in experiments Nos. 3, 5, 6, 7, 8, 9, and 14, 10 ml were taken. In experiments Nos. 5 and 6 only coloration of the solutions was observed; rearrangement products and anilines were not found. The work-up of all these experiments is similar to that described above. When required, the azo compounds were purified by steam distillation.

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