SUBSTITUTION AT HYDRAZO GROUP AND STABILITY OF SOME HYDRAZO COMPOUNDS

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Received October 12th, 1979

The effects of pH and of substitution at the hydrazo group on the rate of disproportionation were studied for some hydrazo compounds. Spectrophotometric investigation of the acid–base equilibria, polarographic measurements, and preparative electroreduction evidenced that the disproportionation is always acid catalyzed. The nonmonotonic dependence of the disproportionation rate on the pH of the solution is due to a change in the electron donor or electron acceptor effect of the substituent resulting from a shift in the acid–base equilibrium between the various forms of the hydrazo compound in question.

Attention has been paid to disproportionation of hydrazo compounds in relation to their polarographic behaviour[1–6]. Polarographic and coulometric measurements and results of preparative electroreduction have evidenced that azobenzene derivatives reduce *via* the corresponding hydrazo compounds, which with different rates undergo the disproportionation.

Florence[7] has examined the effects of substituents and medium on the disproportionation rate. As he has found, protonation of hydrazobenzene derivatives brings about their chemical lability; they are, therefore, stabilized to a different extent by electron acceptor substituents, which is in accordance with the experience of preparative organic chemistry. On the other hand, electron donor substituents, increasing the electron density at the nitrogen atom, favour the protonation of the formed hydrazo compound, which, owing to the effect of H^+ ions, undegoes intramolecular disproportionation associated with cleavage of the molecule to aniline and the corresponding quinoneimine intermediate product[1,7]. The disproportionation rate thus increases with decreasing pH and increasing electron donor effect of the substituents. Polarographic study of pyridylazo, thiazolylazo, and quinolylazo derivatives of phenols and naphthols and their comparison with the benzene analogues has been the subject of the work[8]. Heterocyclic hydroxyazobenzene compounds give two-electron polarographic waves in acidic solutions and four-electron waves only in strongly alkaline solutions, hence the dependence of the wave height on the pH is opposite to that occurring for hydroxyazobenzenes. The relative stability of heterocyclic hydrazo compounds has been explained in terms of the electron acceptor effect of the pyridyl, thiazolyl, or quinolyl group, operating against the electron donor effect of the —OH or $=NH_2$ group. The authors suggest that disproportionation of pyridylhydrazo compounds, in contrast to hydrazobenzenes, is base catalyzed[20]. Disproportionation of hydrazobenzenes is a first order reaction with respect to the H^+ ion concentration.

The purpose of the present work is to characterize the substituent effect on the stability of hydrazo compounds based on a study of the acid–base and polarographic behaviour of eight azo compounds.

EXPERIMENTAL

The substances studied were prepared by diazotization with subsequent coupling under experimental conditions described previously: *I* and *IV* (ref.[9]), *II* (ref.[10]), *III* (ref.[11]), *V—VIII* (refs[12–15]). The hydrazo compounds H *I*—H *VIII* were obtained by preparative electroreduction of the respective azo compounds *I—VIII*. All other chemicals used were of reagent grade purity.

Polarographic measurements were carried out on an OH-102 polarograph (Radelkis, Budapest). Preparative electroreduction was performed as described previously[16]. Spectrophotometric measurements were carried out on a Specord UV-VIS recording spectrophotometer (Zeiss, Jena).

RESULTS AND DISCUSSION

Seeking the relation between the stability of hydrazo compounds and the substituents at the hydrazo group, we confronted the results of spectrophotometric investigation of the acid–base equilibria, results of polarographic measurements, preparative electroreduction, and behaviour of the intermediate products of reduction of the corresponding azo compounds. The results of the study of the acid–base equilibria and preparative electroreduction for the azo compounds *I – VIII* have been reported previously[9].

Polarographic study of the azo compounds *I – VIII* in aqueous-alcoholic Britton–Robinson buffers revealed that the compounds *I*, *II*, *IV*, and *V* reduce in a single cathodic wave over the entire pH region, the compounds *III* and *VI – VIII* reduce, in dependence on the pH, in up to three cathodic waves. In all cases the first cathodic wave corresponds to the reduction of the azo group. As the relative height of this wave shows, the average number of electrons taking part in the first-step reduction of the azo group varies within the range of 2 – 4 (Table I). The non-integral average number of electrons, varying not only in dependence on the azo compound concerned, but also in dependence on the pH, indicates that the azo group does not reduce directly in the four-electron step to the respective amines, but in all cases reduce *via* differently stable two-electron intermediates – the corresponding hydrazo compounds (H *I* – H *VIII*).

Spectrophotometric investigation[9] of the first-step reduction of the azo compounds *I – VIII* has evidenced that over the entire pH region, the corresponding hydrazo compounds undergo in inert atmosphere a single reaction, *viz*. a differently fast

TABLE I

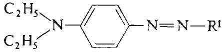
Polarographic Behaviour of the Azo Compounds *I—VIII*

$E_{1/2}$ values against S.C.E.

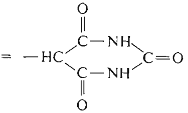
Compound	pH 3·81			pH pH 5·84			pH 7·72			pH 10·27			pH 11·51			pH 13·36		
	$E_{1/2}$ V	i_d nA	n	$E_{1/2}$ V	i_d nA	n	$E_{1/2}$ V	i_d nA	n	$E_{1/2}$ V	i_d nA	n	$E_{1/2}$ V	i_d nA	n	$E_{1/2}$ V	i_d nA	n
I	—0·400	320	4	—	320	4	—	320	4	—0·790	320	4	—	320	4	—1·220	320	4
II	—0·235	320	4	—0·475	320	4	—0·625	320	4	—0·735	300	3·75	—0·780	300	3·75	—0·990	290	3·6
III	—0·325	300	3·75	—0·470	270	3·4	—0·580	220	2·75	—0·710	280	3·5	—0·750	290	3·6	—1·015	300	3·75
IV	—0·430	280	3·5	—0·625	290	3·6	—0·740	310	3·9	—0·855	320	4	—0·920	300	3·75	—	—	—
V	—0·125	200	2·5	—0·285	180	2·2	—0·440	160	2	—0·580	160	2	—0·660	160	2	—0·785	160	2
VI	—0·085	160	2	—0·210	190	2·3	—0·340	160	2	—0·485	160	2	—0·545	160	2	—0·615	160	2
VII	—	—	—	—0·150	210	2·6	—0·270	200	2·5	—0·475	180	2·2	—0·565	160	2	—0·635	160	2
VIII	—0·070	180	2·2	—0·200	200	2·5	—0·360	160	2	—0·565	200	2·5	—0·655	240	3	—0·925	220	2·75

disproportionation to the azo compound and amines. No other reaction, such as isomerization, can be involved, since after the establishment of the equilibrium, the reduced solution contains only a mixture of the azo compound and amines, and after the completed reduction only an equimolar mixture of amines is present[9].

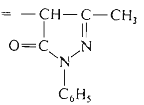
A cathodic wave corresponding to the reduction of the —NH—NH— group is observed only in the case of the substances *VI – VIII*. The hydrazo compound obtained by reduction of the substance *V*, H *V*, is polarographically further not reducible, although its stability with respect to the lifetime of the mercury drop electrode is sufficient.



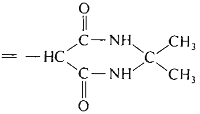
I, R^1 =



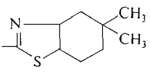
IV, R^1 =



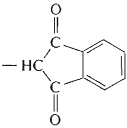
II, R^1 =



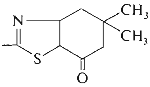
V, R^1 =

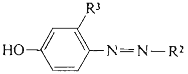


III, R^1 =

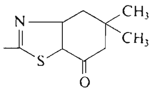


VI, R^1 =



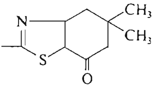


VII, R^2 =



R^3 = H

VIII, R^2 =



R^3 = OH

In acidic solution, the product of preparative electroreduction at the potential of the first cathodic wave is an equimolar mixture of the corresponding amines in all instances except the substance *VI*, from which a comparatively stable hydrazo compound is obtained. As we were able to demonstrate[13,16,17], this hydrazo compound in 1M-H_2SO_4 solution is not susceptible to atmospheric oxidation, and from the point of view of analytical use, its loss resulting from disproportionation is negligible.

In alkaline solutions and inert atmosphere, only the hydrazo compounds H *V* to H *VIII* are relatively stable. For a determination of their disproportionation rates in such solutions, they must be examined over periods longer than the lifetime of the mercury drop. Hydrazo compounds of the thiazole series in alkaline solutions are rapidly oxidized by atmospheric oxygen to the parent azo compounds. The susceptibility of alkaline solutions of these hydrazo compounds to traces of oxygen was so high that it did not allow us to keep them over a sufficiently long period under inert atmosphere. The measurements had to be conducted in excess reductant; alkaline solutions of the azo compounds *V*–*VIII* were reduced with excess sodium dithionite. The losses of the hydrazo compounds resulting from disproportionation were determined so that samples were taken in preselected intervals and the remaining, non-decomposed hydrazo compound was oxidized quantitatively to the azo compound by shaking under air, and the absorbance was compared with that obtained in the starting time point. The reduction of the compounds *V* and *VIII* with sodium dithionite in alkaline solution (associated with decolouration of the solution) took several minutes. After the reduction, the products could not be oxidized back to the azo compounds, hence, because of disproportionation, the hydrazo compounds were no longer present. The compounds *VI* and *VII* were reduced in this manner within several seconds. The disproportionation rate of the hydrazo compound H *VII* in dependence on the alkalinity of the solution is shown in Fig. 1.

In order to establish the effect of the polarity of the medium on the stability of the hydrazo compound H *VII*, we measured its disproportionation rate in dependence on the content of ethanol (Fig. 2). As is evident from Fig. 1, the disproportionation rate at a constant concentration of ethanol increases with decreasing basicity of the solution. The basicity of an NaOH solution can only decrease with increasing content of ethanol. Spectrophotometric measurements proved that even so the basicity is sufficient for the hydrazo compound to be completely dissociated. Regarding the fact that the disproportionation rate of the hydrazo compound H *VII* decreases with increasing content of ethanol (Fig. 2), we must see the cause of the enhanced resistance of the hydrazo compound to disproportionation in a direct effect of the lowered polarity of the medium on the mechanism of disproportionation of the same acid–base form of the hydrazo compound. The properties of the hydrazo compound H *VI* have been described in[17]. A comparison of the rates of disproportionation of the hydrazo compounds H *VI* and H *VII* is presented in Fig. 3.

The effect of substitution at the hydrazo group on the disproportionation rate can be characterized as follows. The average numbers of electrons taking part in the reduction of the azo groups indicate that the hydrazo compounds H *I* – H *IV* disproportionate as rapidly as within the lifetime of the mercury drop (about 3 s)

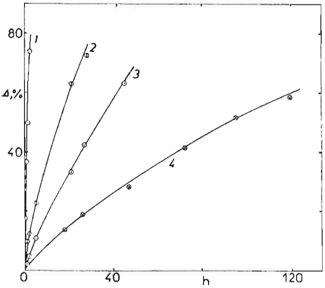


FIG. 1

Loss of the Compound H *VII* Resulting from Disproportionation in Dependence on the Alkalinity of the Medium

$c_{\mathrm{H\,VII}}$ (in time t_0) = $2 . 10^{-5}$ mol l^{-1}, 40% (v/v) ethanol, d = 1 cm. *1* 0·1M, *2* 0·5M, *3* 1M. *4* 2M-NaOH.

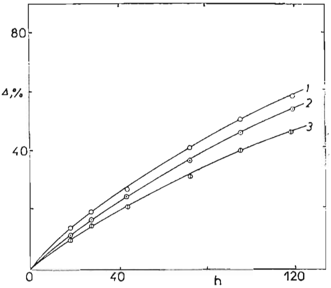


FIG. 2

Loss of the Compound H *VII* Resulting from Disproportionation in Dependence on the Content of Ethanol in 2M-NaOH Solution

$c_{\mathrm{H\,VII}}$ (in time t_0) = $2 . 10^{-5}$ mol l^{-1}, d = 1 cm. *1* 40%, *2* 50%, *3* 60% (v/v) ethanol.

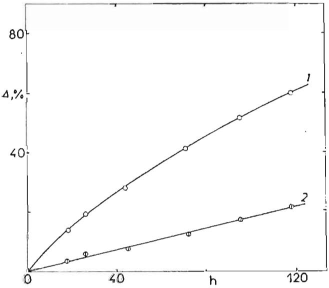


FIG. 3

Loss of the Compounds H *VI* and H *VII* Resulting from Disproportionation in 2M-NaOH in Dependence on Time

$c_{\mathrm{H\,VI}}$ (in time t_0) = $c_{\mathrm{H\,VII}}$ (in time t_0) = $= 2 . 10^{-5}$ mol l^{-1}, 40% (v/v) ethanol, d = 1 cm. *1* H *VII*, *2* H *VI*.

over the whole pH region. The thiazole series hydrazo groups are more stable. The dependence of their disproportionation rate on the pH of the solution is not a monotonic function; this is accounted for by the dual influence of H^+ ions. The rate of disproportionation of an acid–base form of a hydrazo compound increases with decreasing pH of the solution; disproportionation always requires accepting of a proton by the hydrazo group. On the other hand, a shift of the acid–base equilibrium of the hydrazo compound in question can alter the electron density at the hydrazo group, hence its ability to accept a proton; thus acidification of the solution can also bring about an increase in the stability of the hydrazo compound.

Within this concept, the observed dependences can be interpreted as follows. The hydrazo compound H *VI* is stable in 1M-H_2SO_4 owing to the fact that in this solution it is doubly protonized[16]; this is not possible in the case of the hydrazo compounds H *VII* and H *VIII*. In 2M-NaOH solution, the stability of the compound is due to the concentration of H^+ ions being insufficient for protons to be accepted by the hydrazo groups in the disproportionation mechanism[3]. Polarographic measurements in neutral solutions bear out the relative stability of H *VI*, but the product of preparative electroreduction of the compound *VI* is only an equimolar mixture of amines: in fact, protonation of the substituents is no more possible, and the electron density at the hydrazo group for a relatively high concentration of H^+ ions is sufficient for a primary accepting of a proton. In alkaline solutions, the stability of the hydrazo compounds decreases in the order H *VI* > H *VII* > H *V* > > H *VIII*.The values of the half-wave potentials of reduction of the azo groups in the corresponding azo compounds, which are a measure of the electron density at the azo groups, increase also in this order.

The markedly different behaviour of the hydrazo compounds H *V* and H *VI* in acidic solutions, however, indicates that the above explanation cannot be looked upon as complete.

In the paper[18] we have shown that unlike 2-amino-5,5-dimethyl-4,5,6,7-tetrahydrobenzthiazole[19], 2-amino-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzthiazole in acidic solutions exists in the tautomeric imino form. The bands in the UV spectrum of the hydrazo compound H *VI* in acidic solution correspond to those for this amine form[17,20]. Thus the cause of the exceedingly high stability of H *VI* in acidic solution must be sought in the occurrence of the imino form of H *VI* in this medium.

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Translated by P. Adámek.