Oxidation and disproportionation of 2-(*p*-*N*,*N*-diethylaminophenylhydrazo)-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole

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Dedicated to Professor S. Stankoviansky on his 70th birthday

The hydrazo compound studied is not oxidizable by air oxygen in the medium of 2 N-H_2SO_4, but it is instantaneously oxidized by a solution of $K_3Fe(CN)_6$ to give an azo compound. The rate of oxidation by oxygen increases with decreasing acidity and in the medium of 2 N-NaOH it is limited only by the rate of diffusion of oxygen into alkaline solution. In the presence of excess hydrazo compound, two moles of the azo compound arise from two moles of the hydrazo compound and one mole of oxygen. In the presence of excess oxygen, the equimolar amounts of azo compound and hydrogen peroxide are formed. The rate of disproportionation is not a monotonous function of $[H^+]$. It reaches the highest value in neutral medium and is practically negligible in the medium of 2 N-H_2SO_4 or 2 N-NaOH.

Изучаемое гидразосоединение в среде 2 н-H_2SO_4 не окисляется кислородом воздуха, но мгновенно окисляется раствором $K_3Fe(CN)_6$ в азосоединение. Скорость окисления кислородом повышается с понижением кислотности и в среде 2 н-NaOH определяется только скоростью диффузии кислорода в щелочной раствор. При избытке гидразосоединения образуются два моля азосоединения из двух молей гидразосоединения и одного моля кислорода. При избытке кислорода образуются эквимолярные количества азосоединения и перекиси водорода. Скорость диспропорционирования не является монотонной функцией $[H^+]$. Она имеет наибольшее значение в нейтральной среде и практически пренебрежимая как в случае 2 н-H_2SO_4, так и в среде 2 н-NaOH.

The problem of disproportionation of hydrazo compounds was solved in connection with polarographic study of azo compounds especially in [1—5]. *Laitinen* and *Kneip* [1] were concerned with polarographic study of *p*-dimethylaminoazobenzene and found that the corresponding hydrazo compound was subject to disproportionation the rate of which was so high in acid medium that even the height of wave indicated a four-electron reduction. In basic medium, the height of wave corresponds to a two-electron reduction, but coulometric measurements indicate a four-electron reduction. *Florence* [2] studied the influence of substituent and medium on the rate of disproportionation of hydrazo compounds of the hydrazobenzene type and ascertained that this rate increased with electron-donating ability of the substituent and decreasing pH. *Florence* [4] compared the rates of disproportionation of hydrazo compounds of the benzene, naphthalene, pyridine, and thiazole type. The naphthalene azo compounds which possess the —OH or —NH_2 group in *p*-position with respect to the azo group exhibit simple polarographic waves corresponding to a four-electron reduction within the whole pH interval. The *p*-hydroxybenzeneazo compounds give four-electron waves only in acid medium. On the other hand, the pyridyl- and thiazolyl-*p*-hydroxybenzeneazo compounds exhibit two-electron waves in acid medium and four-electron waves in alkaline medium. The first cathodic wave of 2-(*p*-*N*,*N*-diethylaminophenylazo)-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole the reduction mechanism of which was the topic of our preceding study [6] corresponds to two-electron reduction in the whole pH interval.

The aim of this study is to elucidate the mechanism of the oxidation of the investigated hydrazo compound by air oxygen in alkaline medium and on the basis of the results of polarographic and spectrophotometric study and preparative electroreduction to characterize the dependence of the rate of this oxidation and disproportionation on pH of the medium.

Experimental

2-(*p*-*N*,*N*-Diethylaminophenylazo)-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole was prepared according to [6]. 2-(*p*-*N*,*N*-Diethylaminophenylhydrazo)-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole was prepared by preparative electroreduction on a mercury pool cathode at a controlled potential in the region of beginning limiting current of the first cathodic wave ($E = -0.3$ V *vs.* SCE) in the medium of 0.5 N-H_2SO_4 [6]. The stock solution of 20 N-H_2SO_4 was standardized with Na_2CO_3. All chemicals used were anal. grade reagents.

The spectrophotometric measurements were carried out on a spectrophotometer VSU-2P and a recording spectrophotometer Specord UV VIS (Zeiss, Jena). The polarographic measurements were performed in a Kalousek vessel with a polarograph LP 60.

Results and discussion

On the polarogram of 2-(*p*-*N*,*N*-diethylaminophenylazo)-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole (AT) taken in alkaline medium (Fig. 1, curve *1*), we may observe the first cathodic wave (*a*) over which the second poorly developed and imperfectly reproducible wave (*b*) appears in more negative position. However, the product of preparative electroreduction (AT) in alkaline medium at the potential of the beginning limiting current of the first or second wave as well as the product obtained by reduction with sodium amalgam is always the same hydrazo compound (HAT) which is very rapidly oxidized by air oxygen to give the original azo compound. The hydrazo compound (HAT) (Fig. 1, curve *2*) gives a distinct anodic wave the half-wave potential of which is identical with the half-wave potential of the first cathodic wave of AT, which evidences the reversibility of this redox process. Since the second cathodic wave (*b*) cannot be attributed to further reduction of HAT, it must be related with the properties of this hydrazo compound. HAT is very sensitive to traces of oxygen and the variable height of the second cathodic wave is due to this fact. Therefore, we allowed an alkaline solution of HAT to be oxidized by oxygen. Afterwards, we bubbled it through with purified nitrogen and recorded the corresponding polarogram (Fig. 1, curve *3*). It was equal to the polarogram of the corresponding equimolar mixture AT + H_2O_2 (Fig. 1, curve *4*). The alkaline solution of H_2O_2 alone manifests itself only by wave *3c* or *4c*. The interpretation of step (*b*) which is well developed in curves *3* and *4* and poorly developed in curve *1* (Fig. 1) must be based on the following facts. Polarographic step (*b*) corresponds neither to reduction of HAT

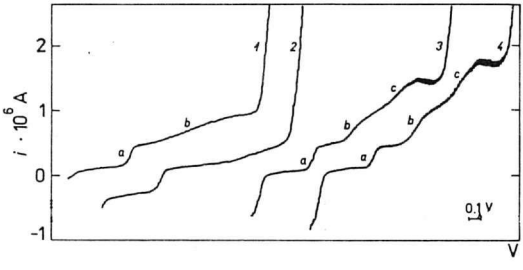


Fig. 1. Polarograms of AT, HAT, HAT + + O_2, AT + H_2O_2.
LP 60, start −0.200 V/SCE, 0.100 V cm^{-1}, sensitivity 1/50, t_{drop} = 3 s, c_{NaOH} = 0.5 N, $c_{C_2H_5OH}$ = 40 volume %.
1. 10^{-4} M-AT; *2.* 10^{-4} M-HAT; *3.* 10^{-4} M-HAT + O_2; *4.* 10^{-4} M-AT + + 10^{-4} M-H_2O_2.

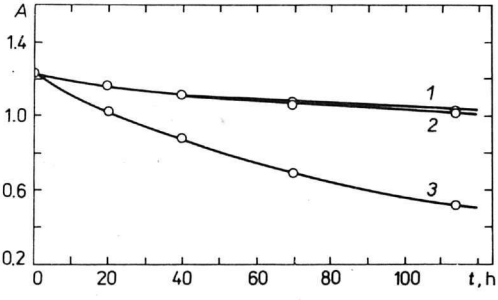


Fig. 2. Loss of HAT due to disproportionation as a function of time in alkaline medium.
$c_{HAT} = 4 \times 10^{-5}$ M, $c_{C_2H_5OH}$ = 40 volume %, d = 0.5 cm.
1. In 2 N-NaOH; *2.* in 1 N-NaOH; *3.* in 0.1 N-NaOH.

nor to reduction of hydrogen peroxide. The condition of its existence is the simultaneous presence of HAT and H_2O_2. As H_2O_2 has an oxidation effect on HAT, step (*b*) is to be attributed to the reduction of an intermediate of this oxidation.

The experiment documented with Fig. 1 as well as the observation that an addition of hydrogen peroxide to HAT in inert medium brings about its oxidation to AT makes it possible to describe the oxidation of alkaline HAT solution with oxygen by the following equations

$$\text{—NH—NH—} + O_2 \rightarrow \text{—N=N—} + H_2O_2 \qquad (A)$$

$$\text{—NH—NH—} + H_2O_2 \rightarrow \text{—N=N—} + 2H_2O \qquad (B)$$

The part of these reactions in the formation of AT is dependent on the concentration ratio of O_2 to H_2O_2. Provided $c_{O_2} \gg c_{HAT} \sim c_{H_2O_2}$ only reaction (*A*) proceeds. If it holds $c_{O_2} < 1/2\ c_{HAT} \sim c_{H_2O_2}$, both reactions take place in full extent so that one mole of oxygen oxidizes two moles of HAT to give two moles of AT.

The hydrazo compound studied is subject in alkaline medium not only to a very rapid oxidation by oxygen but also to a very slow simultaneous disproportionation the rate of which depends on alkalinity of the medium. Because of the possibility of using the reaction of HAT with oxygen analytically, it was necessary at least to estimate the rate of disproportionation as a function of alkalinity of the medium. As we were not able to keep the alkaline solution of HAT in sufficiently inert atmosphere for necessary time interval, we were obliged to measure in the presence of excess reducing agent. A stock alkaline solution of AT was reduced with an excess amount of sodium dithionite. The loss of HAT in it due to disproportionation was determined in convenient time intervals, as follows: A part of the stock solution in a given instant of time was quantitatively oxidized with oxygen (undisproportionated HAT was oxidized to AT). The difference in absorbance in this instant of time and zero time is proportional to the amount of disproportionated HAT in this instant of time. The results of these measurements are represented in Fig. 2. We can see that the rate of disproportionation, which decreases with increasing alkalinity, in the medium of 1 N-NaOH is small enough for a possible practical use of HAT, *e.g.* for the photometric microdetermination of oxygen or for the purification of gases containing oxygen.

In the acid medium, the rate of oxidation by oxygen is incomparably lower than in the alkaline medium. In order to determine the part of disproportionation and the part of oxidation by oxygen in the loss of HAT at varying acidity of the medium, we performed the following measurement: On the mercury pool cathode, we reduced AT to HAT at a controlled potential and we investigated the rate of decrease of the hydrazo compound due to oxidation and that due to disproportio-

nation in the medium of 0.5—3 N-H_2SO_4 by measuring the increase in AT. By determining the value of absorbance (at $\tilde{\nu}_{max}$ AT), we estimated the increase in AT due both to disproportionation and oxidation by oxygen. Simultaneously, in the same time intervals and under equal conditions, we added an excess amount of ferricyanide to the investigated samples. This oxidant oxidized all remaining HAT to AT. The results of this measurement are represented in Fig. 3.

The loss of AT expressed by the difference between the absorbances of AT after the additions of ferricyanide at zero time and at a given time moment (Fig. 3, curves *1*—*4*) is a measure of disproportionation of HAT at that time moment. If we

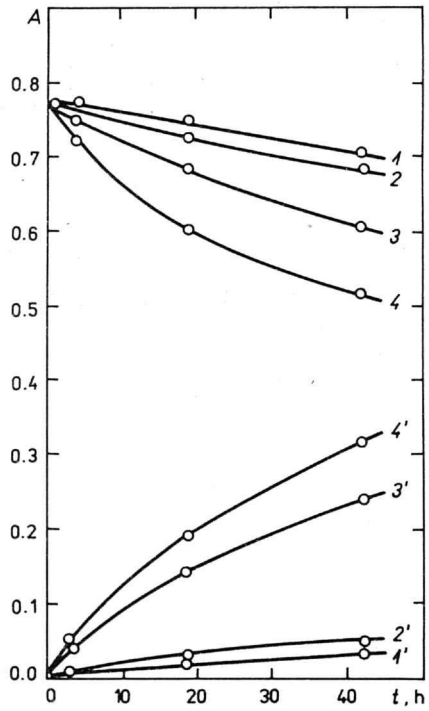


Fig. 3. Loss of AT due to disproportionation of HAT (curves *1*—*4*) and increase in AT due to disproportionation and oxidation of HAT by oxygen (curves *1'*—*4'*) as functions of time in acid media.
Initial $c_{HAT} = 4 \times 10^{-5}$ M, $d = 0.5$ cm.
$c_{H_2SO_4}$: *1.*, *1'*. 3 N; *2.*, *2'*. 2 N; *3.*, *3'*. 1 N; *4.*, *4'*. 0.5 N.

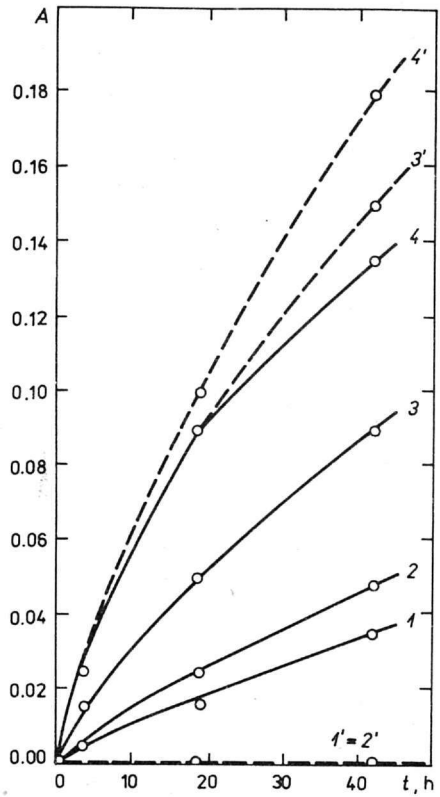
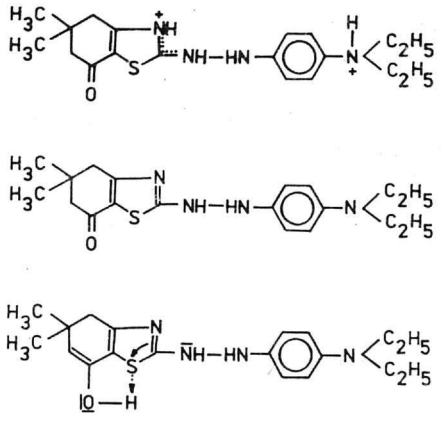


Fig. 4. Increase in AT due to disproportionation (curves *1*—*4*) and increase in AT due to oxidation by oxygen (curves *1'*—*4'*) as functions of time in acid media.
Initial $c_{HAT} = 4 \times 10^{-5}$ M, $d = 0.5$ cm.
$c_{H_2SO_4}$: *1.*, *1'*. 3 N; *2.*, *2'*. 2 N; *3.*, *3'*. 1 N; *4.*, *4'*. 0.5 N.

subtract half of the value of the loss of AT due to disproportionation from the total increase in AT due to oxidation by oxygen and disproportionation (Fig. 3, curves *1'—4'*), we obtain the increase in AT due to oxidation of the hydrazo compound by oxygen. The corresponding plots are represented in Fig. 4.

On the basis of these relationships, we may state that the hydrazo compound HAT is not oxidizable by oxygen in the medium of 3—2 N-H_2SO_4 and is only to a little extent subject to disproportionation. The rate of oxidation by oxygen monotonously and abruptly increases with decreasing acidity of the medium as far as the alkaline region where the rate of oxygen diffusion into solution is the limiting factor. However, the dependence of the rate of HAT disproportionation on the pH is not a monotonous function. The rate of disproportionation rapidly increases in the region from acid to neutral medium where the process is quantitatively completed in the course of 1 or 2 min. Afterwards, it decreases and attains the minimum in strong alkaline medium.

In order to elucidate this behaviour, we recorded the u.v. spectra of the hydrazo compound in acid, weakly acid, and alkaline medium and compared them with the spectra of 2-amino-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole. We found a remarkable consistence. The position of absorption band of the hydrazo compound in the medium of 2 N-NaOH ($\tilde{\nu}_{max} = 26\,000\ cm^{-1}$) is almost identical with the position of absorption band of the corresponding heterocyclic amine ($\tilde{\nu}_{max} = 27\,400\ cm^{-1}$) in this medium. As it has been proved [7] that 2-amino-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole exists in the medium of 2 N-NaOH in the nondissociated enol form stabilized by intramolecular hydrogen bond, we may describe the form of HAT existing in this medium by structure *C*. In neutral medium, the hydrazo compound is so instable that it cannot be used for the



Scheme 1

study of the acid-base forms. In weakly acid medium, HAT exhibits the absorption bands $\tilde{\nu}_{max} = 34\ 000\ cm^{-1}$ and $\tilde{\nu}_{max} = 31\ 000\ cm^{-1}$ instead of the above-mentioned band while only the band $\tilde{\nu}_{max} = 34\ 000\ cm^{-1}$ appears in the medium of 2 N-H_2SO_4. According to [7], the band $\tilde{\nu}_{max} = 31\ 000\ cm^{-1}$ corresponds to the nonprotonated form while the band $\tilde{\nu}_{max} = 34\ 000\ cm^{-1}$ corresponds to the protonated form of the heterocyclic amine. Therefore, we assume that HAT exists in neutral medium in the form which may be described by structure *B*.

Only one form of HAT occurs in the medium of 2—10 N-H_2SO_4. Therefore, the heteronitrogen of the hydrazo compound is quantitatively protonated already in the medium of 2 N-H_2SO_4. As the diethylaminophenylazo compounds of indandione, dimedone, barbituric acid, and pyrazolone are protonated on the nitrogen of the diethylamino group even in weakly acid medium [8], we assume that the protonation of the heteronitrogen is the second degree of protonation of HAT to which structure *A* may be attributed in this medium (Scheme 1).

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