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Coordination Chemistry of Cu^{2+}. II. Correlations between the Structure and Stability of Cu^{2+} Complexes with Antipyrine and 1,10-Phenanthroline, and their Catalytic Effects

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The authors have studied the influence of the structure (electronic and molecular) of the Cu^{2+} - phenanthroline and Cu^{2+} - antipyrine complexes on their catalytic effects in the decomposition of H_2O_2 solutions. The kinetics of the decomposition of H_2O_2 solutions has been studied between 25 and 70°C and the results have been correlated with the π electronic charge, calculated by a simple M.O. method. Some correlations have been made between the stability of the complexes mentioned (I.R. study of the interaction between the various ligands with Cu^{2+}) and catalytic activity, which is more marked for the complexes with antipyrine than for those with phenanthroline. As a result of these correlations definite agreement was found between the estimation of bond strength by the I.R. spectroscopic method, the simple M. O. Hückel calculation, and the kinetic results. The Arrhenius equation applies between 25 and 70°C and the energy of activation is in the range 10-14 kcal/mol.

Introduction

The effect of various complexes on the catalytic decomposition of H_2O_2 solutions has lately been more and more utilized as a method for determining and drawing conclusions about the molecular structure and the nature of bonds in the complexes. The conclusions obtained by studying the variation of catalytic activity as a function of the components of the complex have been confirmed by I.R. and E.S.R. determinations.[1,2]

It is well known that organic compounds such as phenanthroline, antipyrine, and aniline inhibit the decomposition of H_2O_2 catalysed by the Fe^{3+} ion,[3] whereas the Cu^{2+} ion is a strong promoter for this reactions.[4-7] The complexes we have studied in this work comprise a promoter part, copper, and an inhibitor part, the organic remainder (nitrogen bearing organic base). It is therefore of interest to study in more detail the effect of Cu^{2+} complexes on the catalytic decomposition of H_2O_2 solutions.

Experimental technique

A thermostatted glass apparatus has been used for the determination of the oxygen volume resulting from the catalytic decomposition of H_2O_2 solutions.[8]

The authors have studied the action of the complexes [Cuphen*X_2] [9] where X = Cl^-, Br^-, I^-, NO_3^-, SCN^-; [Cuphen]X_2 [10] where X = Br^-, $S_2O_3^{2-}$, bs_2,** ts_2,*** CuX_2 . 2apy,[11,12]**** where X = Cl^-, Br^-, NO_3^- on the catalytic decomposition of 2%, 6%, and 10% H_2O_2 solutions, by Fe Cl_3 solutions. The concentration of the complex solutions in water was always 0.05 *M*. In order to compare the results of the various experiments, the following proportions have been used in all cases: 1 ml Fe Cl_3, 0.05 *M* solution and 1 ml complex solution. The same quantity of free oxygen has been obtained by using 4 ml 2% H_2O_2, 1.33 ml 6% H_2O_2 and 0.81 10% H_2O_2.

In order to calculate the rate constant the reaction was assumed to be of the first order.[13,14] In this case:

$$k = 2.303/t \,.\, \log V_f/V_f - V_x$$

where V_f = volume of oxygen released in the total decomposition of H_2O_2; V_x = volume of oxygen released at time t.

For the I.R. determinations, a « U.R. 10 Carl Zeiss, Jena » apparatus and the K Br disc method have been used.

Results and Discussion

The action of various complexes on the decomposition reaction of H_2O_2 catalyzed by Fe Cl_3 is shown in Table I.

It can be noticed that all the complexes cause a decrease of reaction rate in comparison with the test reaction (first line o fthe table). The complexes

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[1] H. Sigel and U. Mueller, *Helv. Chim. Acta, 49,* 671 (1966).

[2] H. Erlenmeyer, U. Mueller, and H. Sigel, *Helv. Chim. Acta, 49,* 681 (1966).

[3] V. Anderson and J. Taylor, *J. Am. Chem. Soc., 45,* 605 (1921).

[4] A. Bohnson and V. Robertson, *J. Am. Chem. Soc., 45,* 2512 (1923).

[5] A. Bohnson and V. Robertson, *J. Am. Chem. Soc., 47,* 1299 (1925).

[6] V. S. Bail and S. P. Baxendal, *Trans. Faraday Soc., 47,* 662 (1951).

[7] J. I. Walton and J. Filson, *J. Am. Chem. Soc., 54,* 3226 (1932).

* 1.10 phenanthroline; ** benzenesulphonic acid; *** toluensulphonic acid; **** antipyrine.

[8] D. Craciunescu and Al. Fruma, *Rev. Roumanie Chim., 9,* 653 (1969); *15,* 71 (1970).

[9] M. Brezeanu, F. Zalau, O. Constantinescu, and L. Pascanu, *An. Univ. Buc. serie St. Nat., 15,* 139 (1966).

[10] D. St. Block, *Austral. J. Chem., 20,* 2275 (1968).

[11] D. Gopolakrishnan and O. O. Patel, *Indian J. Chem., 5,* 364 (1967).

[12] D. Gopolakrishnan, A. Ravi, and O. O. Patel, *Bull. Chem. Soc. Japan, 1,* 791 (1967).

[13] H. Zell and N. Sigel, *Helv. Chem. Acta, 49,* 870 (1966).

[14] A. Konoplena and L. A. Nikolaev, *Zhur. fiz. Khim., 40,* 442 (1966).

causing a reduced rate constant and which therefore have a marked inhibiting character are obviously very stable owing to the reduced number of Cu^{2+} ions released.

Table I. Rate constants for the catalytic decomposition of H_2O_2 solutions in the presence of various Cu^{2+} complexes at 25°C.

	k, min^{-1} H_2O_2 concentrations		
Test reaction	2%	6%	10%
$FeCl_3$	0.162	0.215	0.245
Complexes			
$[Cuphen(NO_3)_2]$	0.111	0.122	0.130
$[CuphenCl_2]$	0.083	0.092	0.110
$[CuphenBr_2]$	0.060	0.068	0.081
$[CuphenJ_2]$	0.049	0.056	0.069
$[Cuphen(SCN)_2]$	0.040	0.046	0.055
$[Cuphen(S_2O_3)]$	0.047	0.054	0.065
$[(Cuphen)]Br_2$	0.044	0.050	0.057
$[Cuphen](S_2O_3)$	0.031	0.039	0.051
$[Cuphen_2]bs_2$	0.019	0.027	0.041
$[Cuphen_2]ts_2$	0.011	0.016	0.028
$CuCl_2 . 2apy$	0.123	0.133	0.149
$CuBr_2 . 2apy$	0.124	0.135	0.148
$Cu(NO_3)_2 . 2apy$	0.117	0.127	0.138

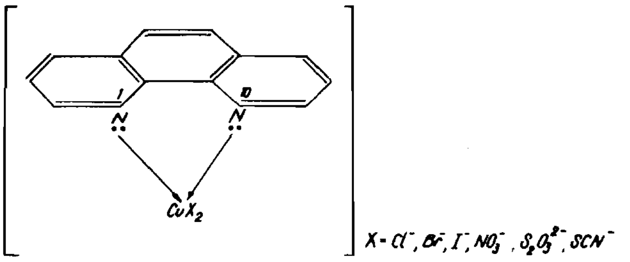


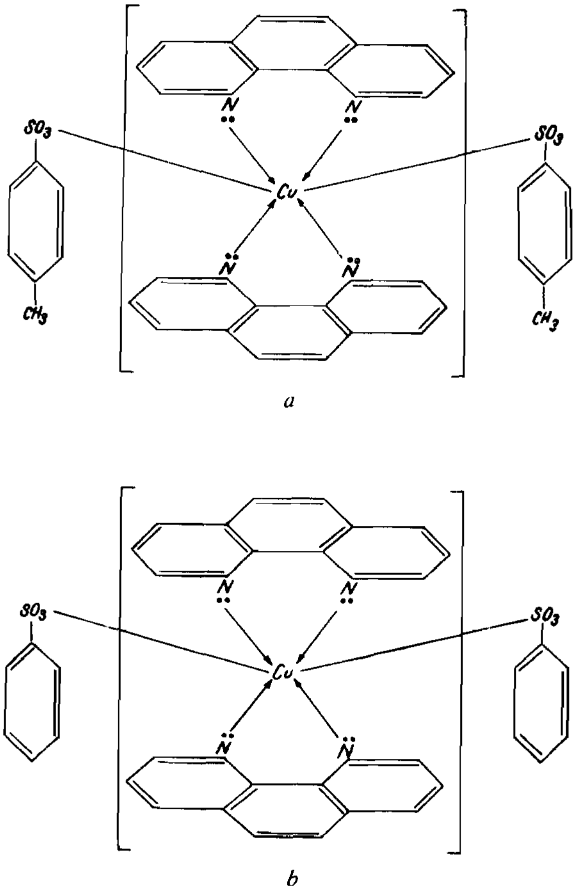
Figure 1. Molecular structure of the $[CuphenX_2]$ complex.

In the $[Cuphen]X_2$ complexes the anion is located outside the copper coordination sphere. The NCu coordinating bond is therefore stronger, copper being weakly involved in the Cu-halogen or Cu-pseudo-halogen bond, than in the case of the $[CuphenX_2]$ complex (Figure 1). This consideration is adequately proved by the rate constant in the presence of the $[CuphenX_2]$ complex which is higher than the one corresponding to the $[Cuphen]X_2$ complex.

I.R. spectroscopy has revealed the existing differences between the C=N vibrations in phenanthroline when the halogen or the pseudo-halogen was located inside or outside the copper coordination sphre (band at 1590 cm^{-1}). This phenomenon is due to the fact that, in complexes of this class, there are only small changes in the stereochemistry of the molecule after complexation (bands at 841 cm^{-1}, characteristic for the vibration of the hydrogen atom existing in the centre of the phenanthroline molecular cycle, are little modified).

In the case of the $[Cuphen(SCN)_2]$ and $[Cuphen(S_2O_3)]$ complexes, an interesting correlation could be established between the observations of the authors who have prepared these complexs[9] concerning the stability of the complexes in water and our own observations in the I.R. spectrum regarding the band centered at 1505 cm^{-1} (characteristic for aromatic compounds). In fact, this band is split to a great extent and its intensity is modified in relation with the other complexes of the same class. This observation suggests greater interaction between the copper atom and phenanthroline than in the case of the other complexes $[CuphenX_2]$. In agreement with this finding, we have obtained experimentally, for the reaction in the presence of the $[Cuphen(SCN)_2]$ complex a small rate constant $k = 0.04$ (for the 2% H_2O_2 solutions). For the $[Cuphen(S_2O_3)]$ complex, the changes in the I.R. bands of phenanthroline, attributed to their aromatic character are important (1425, 1505, and 1590 cm^{-1}). The band attributed to the $S_2O_3^{2-}$ anion stands out more clearly than the bands of the other halogens or pseudo-halogens (540, 670 cm^{-1}). In agreement with the observations of the authors who have synthesised the complex[9] and have proved its high stability, we have obtained very low catalytic activity characterized by a very small rate constant (Table I).

The study of the $[Cuphen_2]bs_2$ and $[Cuphen_2]ts_2$ complexes (Figure 2a and b) has led us to most interesting results. The complexes mentioned above cause a considerable decrease of reaction rate in all H_2O_2 concentrations. We have attributed this decrease to the presence of benzenesulphonic acid and, respectively, of toluenesulphonic acid, as inhibitors,



a

b

Figure 2. *a* and *b* - Structure of $[Cuphen_2]bs_2$ and $[Cuphen_2]ts_2$ complexes.

which both emphasize the importance of the inhibiting groups in the complex, the promoting grouping copper remaining at a constant concentration. The fact that the [Cuphen$_2$]ts$_2$ complex has a lower activity than the [Cuphen$_2$]bs$_2$ complex confirms our observations reported in a previous paper[8] where it was shown that the catalytic activity decreased with the increase of the complex molecular weight in the same class. (For the $CuCl_2 . uNH(C_6H_5)_2$ complexes, where $u = 1, 2, 4, 6$, the catalytic activity decreases with increasing number of coordination positions around Cu^{2+} occupied by the organic ligand, and consequently with increasing molecular weight.

This fact may also be explained from the standpoint of the theory of molecular orbitals. To this end we endeavoured to correlate the electronic density accumulating on the sulphonic grouping with the catalytic activity of the [Cuphen$_2$]bs$_2$ and the [Cuphen$_2$]ts$_2$ complexes. The simple form of the method used by Hückel[15] for the theory of molecular orbitals has been used for computing electronic densities. Thus, the wave function was elaborated in the form of a linear combination of atomic orbitals:

$$\Psi_j = \Sigma C_{ji} \rho_i \qquad (1)$$

where ρ_i represents the six $2p\pi$ atomic orbitals having the benzenic cycle as common origin, a vacant orbital πSO_3H and an orbital πCH_3 proceeding from the CH_3 grouping considered to be a heteroatom[16] and to participate in the conjugation of two electrons.

For the sulphonic grouping the same pattern was used as in a previous paper.[17] The calculation parameters used for the sulphonic grouping were the ones used in the case of benzene sulphinic acid, and for the CH_3 grouping the parameters utilized by Streitwiesser.[18] These parameters result from relation (2).

$$\begin{array}{ll} \alpha_{SO_3H} = \alpha - 2.7\,\beta & \alpha_{CH_3} = \alpha + 2\,\beta \\ \beta_{C_2-SO_3H} = 0.6\,\beta & \beta_{C_6-CH_3} = 0.7\,\beta \\ \alpha_{C_2} = \alpha + 0.2\,\beta & \alpha_{C_6} = \alpha - 0.2\,\beta \end{array} \qquad (2)$$

In relation (2), α and β are Coulomb, respectively, resonance integrals for the carbon atom. The charge densities thus calculated are reported in Figure 3a and b.

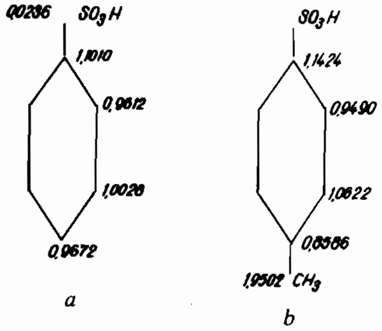


Figure 3. *a* and *b* - Electronic charge calculated for benzenesulphonic acid and for *p*-toluenesulphonic acid.

It now becomes very easy to interpret the kinetic results for the case of the compounds mentioned. Thus, in the case of the benzenesulphonic acid the negative (supplementary) electronic charge, $\rho SO_3H = 2 \sum_{j=1}^{3} C_{ji}^2$ which accumulates on the SO_3H grouping owing to the nature of the conjugation with the benzenic cycle is 0.0236.

In the case of the p-toluene sulphonic acid, which has two substitution groupings of different nature in a position that is best for conjugation, the same charge is

$$\rho SO_3H = 2 \sum_{j=1}^{4} C_{ji}^2 = 0.0254$$

Thus, in the case of the toluenesulphnic acid the electron charge on the SO_3H grouping is considerably increased in comparison with benzenesulphonic acid. This observation suggests a decrease of the catalytic effect in the case of the complex where p-toluenesulphonic acid interferes as a ligand. This is in perfect agreement with the kinetic results in Table I.

The importance of the steric requirements caused by the variation in the anion structure (the presence of the $-CH_3$ extra group in toluenesulphonic acid) is considerable. Unfortunately, we have been unable to detect these steric changes (U.V., I.R. spectra).

A particular class of complexes is the one of $CuX_2 . 2apy$ type where $X = Cl^-, Br^-, NO_3^-$. In these complexes[11,12] the coordinating bond is achieved through the carbonyl grouping of antipyrine (1-phenyl-2,3-dimethylpyrazoline) (Figure 4).

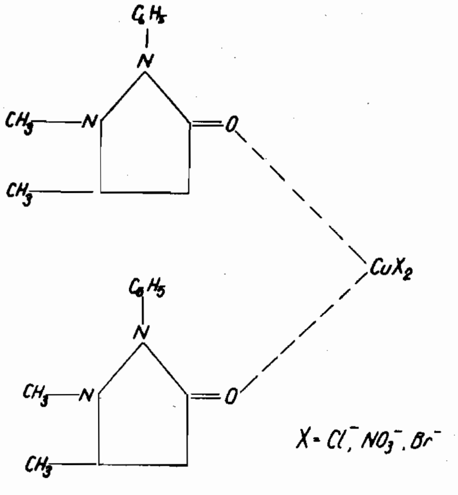


Figure 4. Molcular structure of the $CuX_2 . 2apy$ complexes.

We found that the displacements of the C=O band (about 1666 cm^{-1}) in pure antipyrine are larger for the $CuBr_2 . 2apy$ complex than for the case of the other complexes. The displacement was of 55 cm^{-1}

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(15) N. Hückel, Z. *Phisik*, *70*, 204 (1931).

(16) F. A. Matsen, *J. Am. Chem. Soc.*, *72*, 5243 (1950).

(17) V. E. Sahini, C. J. Ghirvu, and P. Macovei, *Rev. Roumanie Chim.*, *12*, 237 (1967).

(18) A. Streitwiesser jr., «Molecular Orbital Theory for Organic Chemists», J. Wiley & Sons Inc., N.Y. London, 1962, p. 131.

and it should be emphasized that the $CuBr_2 . 2apy$ complex obviously shows a marked reduction of the π character of the double C=O bond. This reduction of π character is larger than for the $CuCl_2 . 2apy$ complex. This explains the high instability of the solution presented by the complexes with Br, and likewise the stronger catalytic effect relative to that for the other $CuX_2 . 2apy$ complexes. The tetrahedral structure of the complex with Br is more distorted than in the case of the $CuCl_2 . 2apy$ complex (this distortion being characteristic for the complexes possessing the bulky molecule of antipyrine). The above considerations could equally explain the lower stability of the $CuBr_2 . 2apy$ complex relative to that of the other complexes with antipyrine.

It should be noticed that, while considerable differences were found among the catalytic effects of the Cu-phenanthroline complexes (the complex with NO_3^- being the most active), the differences are insignificant among the $CuX_2 . 2apy$ complexes, the $Cu(NO_3)_2 . 2apy$ complex being the most inactive; at the same time, the latter possesses a higher catalytic activity than the Cu^{2+} phenanthroline complex.

The variation of the rate constant as a function of the H_2O_2 concentration (Table I) emphasizes the fact that the rate grows in proportion with the increase in concentration of the H_2O_2 solution. Sigel *et al.*[19-21] have noticed a linear dependence of the activity on $[H_2O_2]$. They assumed that an oxidation process does not occur for the copper complexes towards Cu_2O, whose presence was evidenced only 2h after the starting of the reaction. We also failed to observe any prsence of Cu_2O. In conclusion we noticed the increase of the with increasing $[H_2O_2]$. without any postulation of this phenomenon.

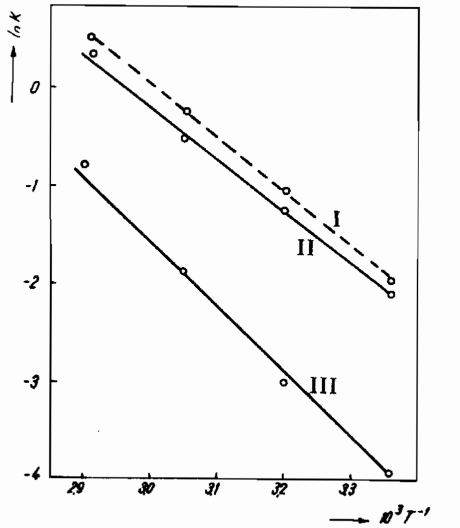

Figure 5. Changes of the rate constant with temperature: I $CuCl_2 . 2apy$. II $[Cuphen(NO_3)_2]$. III $[Cuphen_2]ts_2$.

In order to calculate the activation energy we have carried out experiments at temperatures other than 25°C (Figure 5).

In order to find the range of activation energy, the most active complex $[Cuphen(NO_3)_2]$ and likewise the most inactive complex $[Cuphen_2]ts_2$ (Cu^{2+} phenanthroline complexes) have been studied between 25 and 70°C). We have also studied only the $CuCl_2 . 2apy$ complex (from the Cu^{2+} antipyrine complexes), because the activity of the Cu^{2+}–apy complexes is very similar. The concentration of the H_2O_2 solutions was 6%.

It can be noticed in Figure 5 that the rate constant varies with the increase in temperature according to Arrhenius' equation. If we consider the fact that the various points fit the curves satisfactorily we find that the mechanism of the reaction does not alter. The activation energy thus computed ranged between 10 and 14 Kcal/mol for the complexes of copper with phenanthroline, and was about 11 Kcal/mol for the complexes of copper with antipyrine. The above values are similar to those found in the literature[8,22] for other complexes (9-19 Kcal/mol).

Conclusions

Obvious agreement was found between the results of the computation of the π electronic charge, the catalytic effect of the complexes studied, and certain structural considerations (appreciation of « bond strength ») by I.R. spectroscopic study.

The Cu^{2+} antipyrine complexes have more marked catalytic effect than the Cu^{2+} phenanthroline complexes. The activation energy ranges between 10 and 14 Kcal/mol.

(19) H. Erlenmeyer, C. Flierl, and H. Sigel, *J. Am. Chem. Soc.*, *91*, 1065 (1963).

(20) H. Sigel, C. Flierl, and R. Griesser, *J. Am. Chem. Soc.*, *91*, 1061 (1969).

(21) Th. Kaden and H. Sigel, *Helv. Chim. Acta*, *51*, 947 (1968).

(22) T. V. Vorobieva, M. V. Voevodskii, and A. L. Purmal, *Zhur. Fiz. Khim.*, *36*, 532 (1962).