[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Electronic States of *p*-Benzoquinone[1]

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The absorption spectrum of *p*-benzoquinone has been studied at 20°K. in the crystalline state from 15000 to 35000 cm.$^{-1}$, using single crystals in polarized light. It is concluded that there are at least three distinct n-π^* transitions between 18000 and 25000 cm.$^{-1}$, as well as a π-π^* transition near 30000 cm.$^{-1}$. The n-π^* transitions are very sharp, and partial vibrational analyses are presented. The π-π^* transition is much more diffuse and shows evidence of predissociation in the excited electronic state. The spectra are classified with respect to theoretical calculations and semi-empirical correlations. No fluorescence or phosphorescence was observed. The spectra are compared in detail with the vapor and solution spectra obtained by previous workers.

Introduction

The absorption spectrum of *p*-benzoquinone has been carefully studied by several workers. A very detailed investigation of the absorption spectrum in the vapor and in solution was made in 1926 by Light.[3] Seshan[4] has also studied the absorption spectrum of *p*-benzoquinone and other quinones in the vapor phase, and Nagakura and Kuboyama[5] have measured the absorption spectra and dipole moments of several quinones in solution. In this work the absorption spectrum of single crystals of *p*-benzoquinone at 20°K. is reported, and a comparison is made with previous work.

Experimental

Eastman Kodak *p*-benzoquinone (practical) was purified by steam distillation followed by recrystallization from petroleum ether and was sublimed *in vacuo* before use. Single crystals were prepared by recrystallization from the melt between quartz disks and also by sublimation. The polarized spectra of single crystals at 20°K. were measured with the large Hilger Littrow quartz prism spectrograph at the University of California using Kodak 103-F plates and a 50 μ slit. The crystal was immersed directly in liquid hydrogen. Light sources were a tungsten lamp from 15000 to 26000 cm.$^{-1}$ and a Hanovia high pressure Xenon arc from 26000 to 35000 cm.$^{-1}$. A Wollaston prism behind the slit of the spectrograph produced in the focal plane two spectra of opposite polarization. The crystal was mounted so that one of its extinction directions in the cleavage plane was parallel to the optic axis of the Wollaston. An iron arc was used to record calibration spectra, and a Hartmann diaphragm was used to avoid movement of the plate between exposures of the absorption and calibration spectra. Plate readings were reduced to wave numbers *in vacuo* (cm.$^{-1}$) with a Hartmann dispersion formula which reproduced the iron arc calibration lines to better than 0.2 Å.

The absorption spectrum was also measured in the vapor and in solution in petroleum ether (Mallinckrodt, analytical reagent grade). The measurements of the solution spectra were performed at the University of Rochester, using both Beckman and Cary spectrophotometers.

Experimental Results

The crystal structure of *p*-benzoquinone has been accurately determined by Robertson.[6] The crystal belongs to the monoclinic system, and the space group symmetry is C_{2h} ($P2_1/a$) with two molecules per unit cell. The molecular planes nearly coincide with the $(20\bar{1})$ plane of the crystal. In the $(20\bar{1})$ plane, the long molecular axis (the axis joining the O atoms) makes an angle of 36.9° with the *b*-axis of the crystal. The $(20\bar{1})$ plane is a cleavage plane of the crystal, and the acute bisectrix is nearly perpendicular to the $(20\bar{1})$ plane.[7] Optical examination of the crystals showed that the plane under observation in these experiments was always the $(20\bar{1})$ plane. The *b*-axis was identified by the position of the acute bisectrix figure which is seen in polarized converging monochromatic light. For convenience, the axis which is perpendicular to the *b*-axis in the $(20\bar{1})$ plane will henceforth be referred to as the *p*-axis.

Three distinct regions of absorption are seen in the visible region of the spectrum. These will be discussed individually.

Transition (a).—A very weak absorption system is seen from 18942 to 20061 cm.$^{-1}$. The absorption is more intense in the *p*-axis than in the *b*-axis. The lines of this system are given in Table I and can be seen in the microphotometer tracing in Fig. 1.

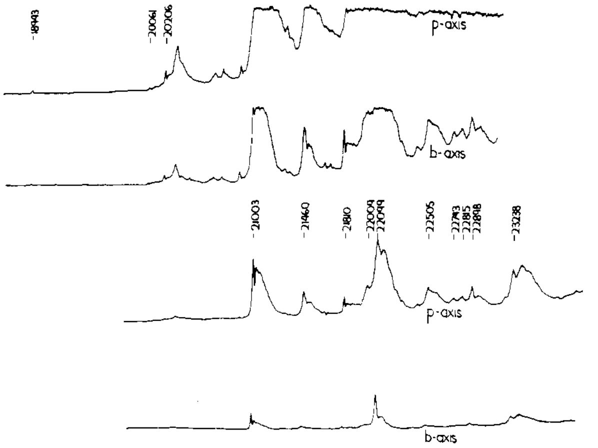

Fig. 1.—Microphotometer tracing of the polarized absorption spectrum of *p*-benzoquinone crystal in the visible region. $(20\bar{1})$ plane; 20°K. The crystal used to record the upper two spectra is thicker than the crystal used to record the lower two spectra. The frequencies are in cm.$^{-1}$. and are accurate to 2 cm.$^{-1}$.

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[2] Postdoctoral Fellow under a grant by The Shell Fellowship Committee to the Department of Chemistry of the University of Rochester, 1955–1956.

[3] L. Light, *Z. physik. Chem.*, **122**, 414 (1926).

[4] P. K. Seshan, *Proc. Ind. Acad. Sci.*, **3A**, 172 (1936).

[5] S. Nagakura and A. Kuboyama, THIS JOURNAL, **76**, 1003 (1954).

[6] J. M. Robertson, *Proc. Roy. Soc.* (*London*), **A150**, 106 (1935).

[7] P. Groth, *Chem. Kryst.*, **4**, 140; G. Caspari, *Proc. Roy. Soc.* (*London*), **A136**, 82 (1932), has shown that the planes labeled as (1*kl*) by Groth are really (2*kl*).

Transition (b).—An absorption system which is somewhat more intense than system (a) is seen from 20206 to 20894 cm.$^{-1}$ in the tracing in Fig. 1. The lines of this system, which are more intense in the *p*-axis polarization, are given in Table II.

TABLE I

TRANSITION (a) OF *p*-BENZOQUINONE CRYSTAL, 20°K.

Rel. intensity	ν, cm.$^{-1}$, ±2	Assignment
s	18942	Origin of analysis, $^3U \leftarrow {}^1A$
vw	18973	31, lattice
vw	19008	2(31); 65, lattice(?)
vw	19047	65 + 31
vw	19084	Lattice
vw	19360	418, skeletal deformation, Ag
m	19751	809, skeletal deformation, Ag
vw	20024	1082, skeletal deformation or stretch, Ag
s	20061	1119, C=O stretch (?), Ag
vw	20096	1119 + 31

TABLE II

TRANSITION (b) OF *p*-BENZOQUINONE CRYSTALS, 20°K.

Rel. intensity	ν, cm.$^{-1}$, ±2	Assignment
s	20206	Origin of analysis, $^1U \leftarrow {}^1A$
w	20236	30, lattice
vs	20289	83, lattice
vs	20313	30 + 83
w	20361	2(83)
w	20400	30 + 2(83)
m	20444	(?)238, skeletal deformation, Ag
w	20473	238 + 30
vw	20502	238 + 2(30)
w	20635	
w	20669	
ms	20738	(?) 532, skeletal deformation, Ag
w	20764	532 + 30
w	20821	532 + 83
w	20848	532 + 83 + 30
w	20872	532 + 83 + 2(30)
s	20890	(?) 684, skeletal deformation, Ag
w	20912	684 + 30

Transition (c).—A more intense absorption system is seen from 21003 to 25040 cm.$^{-1}$. This absorption is also more intense in the *p*-axis polarization. The lines are given in Table III, and the tracing of this system is shown in Fig. 1.

In addition to these absorption systems in the visible region, spectra recorded with the thinnest crystals which could be obtained by crystallization from the melt show broad structure in the ultraviolet region of the spectrum.

Transition (d).—A much stronger absorption system is seen in the vicinity of 30000 cm.$^{-1}$. The bands of this system are much broader than the sharp lines found in the visible region. The absorption is more intense in the *p*-axis polarization. The intensity increases continuously toward higher energies. The frequencies of the broad maxima are listed in Table IV, and a microphotometer tracing is shown in Fig. 2.

The very strong absorption shown by *p*-benzoquinone at 41000 cm.$^{-1}$ (ϵ = 20900) could not be measured in the crystal, since the thinnest obtainable crystals were opaque above 33400 cm.$^{-1}$.

The absorption spectrum of *p*-benzoquinone in petroleum ether is shown in Fig. 3 from 6000 to 3400 Å.

TABLE III

TRANSITION (c) OF *p*-BENZOQUINONE CRYSTAL, 20°K.

Rel. intensity	ν, cm.$^{-1}$, ±2	Assignment
vs	21003	Origin of analysis, $^1U' \leftarrow {}^1A$
vs	21031	30 lattice
vs	21064	2(30)
s to w	<21200	Complex lattice structure
w	21212	
vw	21297	
vw	21343	
ms	21468	457, skeletal deformation, Ag
m	21499	457 + 30
m	21520	457 + 2(30)
w	21647	
w	21680	
vw	21701	
vw	21775	
ms	21810	807, skeletal deformation, Ag
m	21838	807 + 30
m	21895	
m	21941	
w	21980	
ms, broad	22009	1006, skeletal deformation or stretching, Ag
vvs	22094	1091, C=O stretching (?), Ag
vs	22129	1091 + 30
vs	22159	1091 + 2(30)
s	22213	Lattice structure
m	22269	Lattice structure
w	22316	
w, broad	22446	1006 + 457
m, broad	22500	1091 + 457
w, broad	22743	
w, broad	22821	1006 + 807
m	22898	1091 + 807
m	22929	1091 + 807 + 30
w	22959	1091 + 807 + 2(30)
w	23024	
m	23113	1091 + 1006
w	23172	
s	23238	2(1091)
ms, broad	23319	
m, broad	23374	
m to w, broad and complex	>25100	

TABLE IV

TRANSITION (d) OF *p*-BENZOQUINONE CRYSTALS, 20°K.

Rel. intensity	ν, cm.$^{-1}$, ±30	Assignment
vw	30110	Origin of analysis, $^1L_b \leftarrow {}^1A$
w	30620	(?)540, skeletal deformation, Ag
m	31240	2(540)
s	31700	3(540)
vs	32180	4(540)
vvs	32720	5(540)
vvs	>33000	

Discussion and Interpretation

1. **Assignment of the Electronic Transitions.**—The interpretation of the spectrum is facilitated by a comparison of the same electronic transition in different media and by a comparison of the electronic transitions of *p*-benzoquinone with the re-

TABLE V

EFFECT OF THE ENVIRONMENT ON THE ELECTRONIC TRANSITIONS ON *p*-BENZOQUINONE

	Vapor[4]	In hexane[2]		In petroleum ether		In ether[5]		In ethanol[2]		Crystal, 20°K.
	ν	ν	ϵ	ν	ϵ	ν	ϵ	ν	ϵ	ν
(a)		18560	1.4	18550	0.4					18942
		19020	1.5	(?) 19040	0.4					19360, 19751
										20061
(b)	20318	20000	12	19950	4.2	20080	12.3	21800	14.5	20206
	21128	21810	15	20870	11.1	20880	19.9	(Hidden)		(Hidden)
(c)	21013	21850	19.6	21880	21.7	21910	40.7	22900	17.4	21003
	21460	22250	14.5	22310	15.8					21460
	21850	22600	11.2	22670	14.2					21810
	22082	22990	16.8	23030	20.4	23010	40.7	24100	13.5	22094
	22529	23460	13.5	23410	15.8					22505
	22921	23800	9	23800	13.1					22898
	23232	24180	12.6	24260	13.9					23238
	23685	24660	9.5	24680	11.5					
				25440	8.8					
(d)	(31780 + 450n −230p)[4]	36000	350 (max)			36000	1800 (max)	36000	1000 (max)	(30110 + 540n)

lated electronic transitions in toluquinone and *p*-xyloquinone. The effect of the environment on the frequency and intensity of the transitions of *p*-benzoquinone is revealed by an examination of Table V. The correspondence between the prominent maxima in solution and in the crystal is fairly unambiguous. The correspondence between the vapor spectra and the solution and crystal spectra is clear for transition (c) but must be considered uncertain for transitions (b) and (d). The solvent effect of diethyl ether on the relative intensities indicates that (b) and (c) must be due to different electronic transitions.

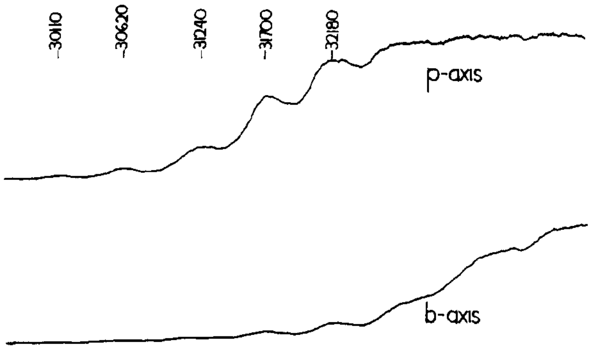

Fig. 2.—Microphotometer tracing of the polarized absorption spectrum of *p*-benzoquinone crystal in the near ultraviolet region. (20$\bar{1}$) plane; 20°K. The frequencies are in cm.$^{-1}$.

The low value of ϵ and the blue shift of the visible absorption transition of *p*-benzoquinone in the solvent sequence petroleum ether, ethanol and water has been interpreted by Nagakura and Kuboyama as evidence for the n-π^* nature of the transition.[5] Further support for this interpretation is given by the effect of methyl substitution, as is seen in a comparison of the maxima of transition (c) in *p*-benzoquinone, toluquinone and *p*-xyloquinone.[3] The reasons for the blue shift in n-π^* transitions when a hydrogen atom in the molecule is replaced by an electron-donating substituent such as methyl or chlorine have been discussed by Orgel.[8]

It is convenient to classify the electronic transitions of a polyatomic molecule in a manner which indicates the similarities between the spectra of different molecules as well as the symmetry properties of the electronic states of the particular molecule. The over-all intensity of the transition depends to a great extent on the symmetry of the local effective field in the vicinity of the chromophoric group, whereas the detailed vibrational structure is governed by the symmetry of the combining electronic states which are classified with respect to the symmetry properties of the entire molecule. Thus, in biacetyl, the over-all intensity of the lowest singlet-singlet n-π^* transition is quite low ($\epsilon \cong$ 20), but the vibrational analysis of the absorption and fluorescence spectra of crystalline biacetyl at 4°K. indicates that the transition is formally allowed by symmetry.[9]

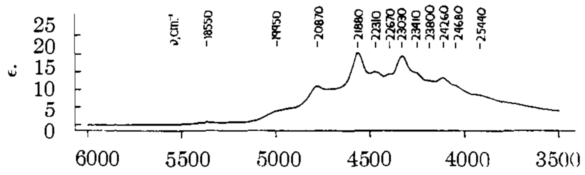

Fig. 3.—Cary recording spectrophotometer tracing of the absorption spectrum of *p*-benzoquinone in petroleum ether in the visible region.

Since no fluorescence or phosphorescence could be detected when *p*-benzoquinone in the crystalline state at 20°K. or in a glassy solution at 77°K. was illuminated with either blue or ultraviolet light from a high pressure mercury arc, it is difficult to determine experimentally whether or not any of the transitions are formally allowed by symmetry. The very low intensity of transition (a) and its position relative to transitions (b) and (c) indicate that transition (a) is probably a singlet-triplet transition. Subject to possible verification by Zeeman effect studies, the very weak transition (a) is tentatively assigned to a singlet-triplet n-π^* transition. A comparison with the corresponding transition in

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[8] L. E. Orgel, *J. Chem. Soc.*, 121 (1955).

[9] J. W. Sidman and D. S. McClure, THIS JOURNAL, **77**, 6461 6471 (1955).

biacetyl also supports this assignment.[9] The low intensity of transitions (b), (c) and (d) indicates that they are probably singlet-singlet transitions which are forbidden by the local effective symmetry and which may or may not also be forbidden by the over-all molecular symmetry. Transition (d) is π-π^* in nature, whereas the transitions in the visible region are n-π^*. According to LCAO-MO calculations by Nagakura and Kuboyama, the lowest unfilled π^* orbital of *p*-benzoquinone belongs to the b_{2g} representation of symmetry group D_{2h}.[10]

The two non-bonding (n) molecular orbitals derived from the p-orbitals of the oxygen atoms are seen to belong to the b_{2u} and b_{3g} representations. The one-electron n-π^* transitions $b_{2u} - b_{2g}$ and $b_{3g} - b_{2g}$ are both forbidden by symmetry in the free molecule. If it is assumed that these orbital transitions correspond to the n-π^* transitions in the visible region of the spectrum, then the singlet-singlet transitions (b) and (c) are forbidden both by local and by molecular symmetry in the free molecule. Although the $b_{2u} - b_{2g}$ orbital transition is formally allowed in the lower symmetry of the crystal (C_{2h}), the overlapping of transitions (a), (b) and (c) precludes a more detailed analysis of the spectrum.

Nagakura and Kuboyama's calculations indicate that the highest filled π MO belongs to representation b_{1g}. The one-electron π-π^* transition $b_{1g} - b_{2g}$ is forbidden by symmetry. This orbital transition probably corresponds to transition (d), which is therefore forbidden both by local and by molecular symmetry. The long progression of a single vibration with increasing intensity indicates that the equilibrium nuclear configuration must be quite different in the upper and lower states of transition (d). The large change in molecular geometry and the diffuseness of transition (d) in both vapor and crystal suggest that predissociation may occur in the excited state.

If transitions (b), (c) and (d) are forbidden by symmetry, the intensity of these transitions is derived from vibrational-electronic interaction. In the absorption spectra of single crystals, the intensity of all four transitions is greater in the *p*-axis polarization than in the *b*-axis polarization. This suggests that the perturbing state is the same in all cases and is very probably the upper state of the very strong transition ($\epsilon = 20900$) at 41000 cm.$^{-1}$. The polarization results are qualitatively consistent with a short-axis, but not with a long-axis, transition moment for the 41000 cm.$^{-1}$ transition, which then necessitates a $^1B_{2u} \leftarrow {}^1A_g$ assignment. According to the MO calculations,[10] the lowest allowed π-π^* orbital transition is $b_{3u} - b_{2g}$, which corresponds to a $^1B_{1u}$, rather than to a $^1B_{2u}$, upper state. However, configurational interaction may change the order of the higher excited states, so that a more refined calculation would be needed in order to check this important point. It might also be necessary to change the assignments given in this paper if an ASMO-CI calculation were to change the order of the lower excited states.

Platt[11] has formulated a notation which is useful for correlating the electronic spectra of molecules. According to Platt's notation, the low-energy n-π^* transitions which are forbidden by the local symmetry of the C=O group and which are therefore of low intensity are U $\leftarrow$ A transitions; the corresponding transition in McMurry's notation is E $\leftarrow$ N.[12] Thus, in Platt's notation, transition (*a*) is $^3U \leftarrow {}^1A$, transitions (b) and (c) are $^1U \leftarrow {}^1A$ and the weak, locally forbidden π-π^* transition (d) is $^1L_b \leftarrow {}^1A$.[13]

2. Interpretation of the Vibrational and Lattice Structure.—Only a very few lines of transition (a) can be seen before it is overlapped by transition (b). The vibrational analysis is therefore quite tentative. The origin of the vibrational analysis is the line at 18942 cm. Lattice modes of 31, 66 (2 × 31?) and 105 cm.$^{-1}$ appear as fine structure in the transition. Vibrations of 809 and 1119 cm.$^{-1}$ appear with moderate intensity, and vibrations of 418 and 1082 cm.$^{-1}$ appear more weakly. In transition (c) the lattice structure is quite complex. At least one lattice mode of approximately 30 cm.$^{-1}$ appears prominently, and other lattice modes may also be active in the transition. The vibrational analysis of transition (c) is not entirely satisfactory. The line at 21003 cm.$^{-1}$ is assigned to the origin of the analysis. The most prominent vibrational interval is 1091 cm.$^{-1}$, which may correspond to the Ag C=O stretching frequency in the upper electronic state. Vibrations of 457, 807 and 1006 cm.$^{-1}$ also appear. However, the calculated value of the combination (1091 + 457) is 46 cm.$^{-1}$ higher than the band to which it is assigned, whereas the calculated value of 2 (1091) is 53 cm.$^{-1}$ lower than the band to which it is assigned. The calculated value of (1091 + 807) is in satisfactory agreement with the assigned band. No definite explanation can be given at present for these discrepancies. It is possible that they are due to perturbations by neighboring molecules in the crystal.

Transition (b) in the crystal is overlapped so closely by transition (c) that a vibrational analysis is impossible. The origin is probably close to the line at 20206 cm.$^{-1}$.

The bands of transition (d) are much broader than the lines found in transitions (a), (b) and (c). The first band is at 30110 cm.$^{-1}$ and a single vibration of 540 ± 30 cm.$^{-1}$ forms long progressions.

Since all transitions in the crystal at 20°K. originate from the lowest level of all vibrations in the ground electronic state, and since rotational structure is absent, the vibrational analysis of the crystal absorption spectrum is simpler than the analysis of

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(10) S. Nagakura and A. Kuboyama, *J. Chem. Soc. Japan*, **74**, 499 (1953). In the convention used by these authors, the molecular plane is the *yz*-plane and the axis joining the two oxygen atoms, *i.e.*, the long axis, is the *z*-axis. Their group-theoretical notation follows the convention of Eyring, Walter and Kimball, "Quantum Chemistry," McGraw-Hill Book Co., New York, N. Y., 1944.

(11) J. R. Platt, *J. Opt. Sci. Amer.*, **43**, 252 (1953).

(12) H. L. McMurry, *J. Chem. Phys.*, **9**, 241 (1941).

(13) The intensity of transition (a) ($\epsilon = 0.4$) is in the range of the $^3W \leftarrow {}^1A$ transitions, rather than the $^3U \leftarrow {}^1A$ range, according to the diagram in reference 11. This transition is classified here as $^3U \leftarrow {}^1A$, since the upper state is very likely derived from the same orbital configuration which gives rise to one of the ^1U states. The intensity of the spin-forbidden transition is due to spin-orbit perturbation of the ^3U state by a higher singlet state. The perturbing state may be a ^1W state, which probably lies above 50000 cm.$^{-1}$. This could then account for the intensity of the $^3U \leftarrow {}^1A$ transition, since spin-orbit coupling would give the ^3U state some ^1W character.

the vapor absorption spectrum. Light has given a vibrational analysis of transition (c) in the vapor in which he has concluded that excited state vibrations of 1110 and 662 cm.$^{-1}$ appear in the spectrum. The vibrational analysis of the crystal absorption spectrum is not in agreement with this, since vibrations of 457, 807, 1006 and 1091 were found. As is seen in Table V, a correspondence between many of the bands in transition (c) may be found by comparing vapor and crystal absorption spectra, so that the analysis which is proposed in this work is not inconsistent with the bands observed in the vapor spectrum.

Seshan[4] has studied transition (d) in the vapor and has found two sets of equally spaced bands, each having a 450 cm.$^{-1}$ spacing with a 230 cm.$^{-1}$ separation between corresponding members of the two sets. These bands are represented by the formula $\nu = 31780 + 450n - 230p$. The crystal absorption bands in this region are much more diffuse than the vapor absorption bands, and it is therefore difficult to state whether the 540 cm.$^{-1}$ interval deduced from the vibrational analysis of the crystal spectrum corresponds to the 450 cm.$^{-1}$ interval in the vapor spectrum.

Seshan has also found a series of very broad bands between 41000 and 45000 cm.$^{-1}$ with an average spacing of 450 cm.$^{-1}$. These bands correspond to the intense transition ($\nu_{\max}$ 41000, $\epsilon_{\max}$ 20900), which must therefore be π-π^* in nature.

A complete vibrational assignment for *p*-benzoquinone would be of considerable assistance in correlating vibrations in the ground and in the excited electronic states as has been done for biacetyl.[9] A more detailed interpretation of the vibrational structure of the absorption transitions must therefore await further work on this molecule.

Acknowledgments.—I am grateful to Dr. S. Nagakura and to Prof. J. R. Platt for helpful discussions concerning the assignment of the electronic transitions. The interest of Prof. D. S. McClure and Prof. A. B. F. Duncan is also acknowledged.

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Metal Interaction with Sulfur-containing Amino Acids. II. Nickel and Copper(II) Complexes[1]

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The formation constants of the nickel(II) complexes of cysteine, glycine and cysteine esters have been measured and compared. The data indicate that the predominant binding sites in cysteine to nickel ion are the amino group and sulfhydryl ion. This interpretation is supported by the identical absorption spectra of the nickel(II) complexes of cysteine and cysteine ester. The rates of alkaline hydrolysis of glycine and cysteine esters have been determined in the absence and presence of metal ions and it was found that in every case an increase in the stability of metal–ester complex is accompanied by an increase in the bimolecular rate constant. The copper(II) complex of oxidized glutathione (GSSG) has been investigated polarographically in the region +0.01 to −0.01 v. (S.C.E.). GSSG forms only a 1:1 complex with copper ion: log $k_1 = 14.6$. This value is close to the log k_1k_2 value (15.1) of the copper complex of glycine and suggests that the binding sites in the GSSG complex are the two amino and α-carboxylate groups.

As part of a program of investigation of metal interaction with sulfur-containing amino acids,[2] studies were carried out to determine the sites of binding in cysteine to nickel ion. The rates of alkaline hydrolysis of glycine and cysteine esters in the absence and presence of various metal ions were investigated in order to determine the relationship between the stability of the metal–ester complexes and the bimolecular rate constants.

Li, Gawron and Bascuas[3] have suggested that in the zinc ion complex of oxidized glutathione (GSSG), the binding sites in GSSG are probably the two amino and α-carboxylate groups. Their postulated structure for the complex is based on a comparison of the value, log $k_1 = 7.22$, for this complex with the values, log $k_1k_2 = 9.96$ and log $k_1k_2 = 8.10$, for the zinc complexes of glycine and valine, respectively. Since there are such big differences in the values of these constants, we considered it worthwhile to study the GSSG complex with another metal ion; the copper(II) complex was investigated polarographically.

Experimental

Materials.—Cysteine methyl ester hydrochloride was prepared and purified in the manner described previously.[2] Oxidized glutathione, a Schwarz product, was dried *in vacuo* at 56° to constant weight. All other chemicals were C.P. reagent grade products. Stock solutions of copper(II) nitrate were analyzed by addition of excess KI and titration of the liberated iodine, stock solutions of nickel nitrate by precipitation with dimethylglyoxime.

Aqueous solutions were prepared from oxygen-free water and all measurements involving sulfur-containing compounds were carried out under an atmosphere of nitrogen. Only freshly prepared stock solutions of these were used.

Apparatus and Procedure.—Polarograms were obtained with a Sargent Recording Polarograph, Model XXI. Two potential measurements were made with an external potentiometer, after stopping the instrument, at points on the wave before and after half-wave potential. The half-wave potential was corrected for *iR* drop, using the minimum cell resistance value measured with a 60 cycle a.c. conductivity bridge. The characteristics of the capillary were: $m = 2.33$ mg. sec.$^{-1}$, $t = 3.74$ sec. (open circuit), at a height of the mercury column of 50 cm.

Measurements of *p*H were made in the apparatus and in the manner previously described.[2] Spectrophotometric

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[1] This investigation was supported by research grants from the National Science Foundation and the American Philosophical Society.

[2] N. C. Li and R. A. Manning, THIS JOURNAL, **77**, 5225 (1955).

[3] N. C. Li, O. Gawron and G. Bascuas, *ibid.*, **76**, 225 (1954).