LiAlH$_4$ Reduction of "Pentaphenylchromium Hydroxide."—The "hydroxide" (0.0031 g.) was reduced with 0.020 g. of LiAlH$_4$ in 40 ml. of ether according to the general procedure previously described in detail. The reaction mixture was hydrolyzed with 0.5 ml. of water after the solution had come clear with the formation of the white precipitate. This precipitate, after separation by filtration, was dissolved in 1 ml. of dilute hydrochloric acid. This solution was saturated with sodium chloride and then extracted with 20 ml. of ether. The ether extract was combined with the ether filtrate, this solution washed with 3% sodium hydroxide twice, and the resultant ether solution was then distilled through the Vigreux column. No benzene was detected in the distillate, but biphenyl was left as residue, 0.0010 g., or 47% of the theoretical amount based on the bis-biphenyl-chromium phenoxide formulation. The alkaline solution was acidified and extracted exhaustively with ether. This ether solution absorbed at 273 mμ and was estimated to contain 0.0003 g. of phenol, or 47% of the theoretical amount.

LiAlD$_4$ Reduction of "Tetraphenylchromium" Iodide.—A solution of 0.0945 g. of the iodide was reduced with 0.200 g. of lithium aluminum *hydride* in 500 ml. of ether for 7 hr. and then hydrolyzed with 2 g. of *deuterium oxide*. After handling this mixture as already described, the ether solution was distilled, and no benzene was detected in the distillate. Biphenyl, 0.0122 g., was obtained by sublimation of the residue, 0.0310 g. (52%) and contained 0.31 D%.[8]

In a completely similar experiment 0.0520 g. of the iodide was reduced with 0.1500 g. of lithium aluminum *deuteride* in 260 ml. of ether. This mixture was hydrolyzed with 1.5 g. of deuterium oxide. Again, no benzene was found in the ether distillate, and biphenyl, containing 5.0 D%,[8] was obtained, 0.0083 g. , by the sublimation of the residue, 0.021 g. (64%), from the distillation.

Biphenyl (100 mg.) was treated with 500 mg. of lithium aluminum *deuteride* in 500 ml. of ether and hydrolyzed with 2.0 ml. of water. The sublimed biphenyl product contained 0.00 D%.[8]

LiAlD$_4$ Reduction of "Triphenylchromium" Iodide.—This iodide (0.300 g.) was reduced with 0.900 g. of lithium aluminum *deuteride* (97.8%) in 1500 ml. of ether and the solution hydrolyzed with 5 ml. of deuterium oxide. The ether solutions from the work-up procedure were distilled through the Vigreux column leaving 0.0890 g. of residue (79%) which gave 0.0470 g. of sublimed biphenyl. The ether distillate contained 0.0162 g. of benzene by spectrophotometric analysis, or 28% of the theoretical amount based on the benzene-biphenyl-chromium iodide structure. The biphenyl obtained above contained 6.7 D%. In a duplicate run made two weeks later the content was found to be 6.55 D%.[8]

DAYTON 7, OHIO

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, DOJINDO & CO., LTD., JAPAN]

Infrared Absorption Spectra of *o*-Hydroxyazobenzene and its Metal Chelate Compounds

BY KEIHEI UENO

RECEIVED DECEMBER 17, 1956

The infrared absorption spectra of *o*-hydroxyazobenzene and its Cu, Ni and Co chelates are reported. Disappearance of the OH band in 3300 cm.$^{-1}$ region and the bathochromic shift of the carbonyl band in 1600 cm.$^{-1}$ region indicate the presence of a resonating system involving the azo linkage and the *o*-hydroxy group. The carbonyl band and the azo band shift to lower frequencies in the metal chelates, and the extent of shift is in the order of Cu > Ni > Co.

Introduction

In connection with an infrared absorption study of polyazobenzenes,[1] an investigation of a series of *o*-hydroxy azo compounds has been undertaken. In spite of the need for fundamental information on infrared absorption spectra of aromatic azo compounds, very little work has been reported in this field. It is the purpose of this investigation to study the infrared absorption spectra of *o*-hydroxyazobenzene, the simplest of the *o*-hydroxy aromatic azo compounds, and its Cu, Ni and Co chelates. The result of such a study should be of importance in connection with infrared analysis of *o*-hydroxy azo dyes of more complicated structures.

Experimental

Preparation of Samples.—*o*-Hydroxyazobenzene was prepared by coupling diazotized aniline with phenol according to the method of Bamberger[2] and was purified *via* copper chelate and recrystallized from ethanol (m.p. 82.5°).

The metal chelates were prepared by refluxing an ethanol solution of ligand and metal acetate for 10 minutes. After cooling, the metal chelates separated as needles, which were then recrystallized from ethanol. Although an attempt was made to prepare the cadmium chelate, only the ligand was recovered. The copper chelate was most easily prepared, while the nickel and cobalt complexes were prepared with increasing difficulty. The metal content of these chelate compounds was determined by complexometric titration after decomposing the samples with fuming nitric acid in a sealed tube,[3] and all the chelate compounds were found to contain 2 moles of ligand per mole of metal. The properties and the result of analyses are shown in Table I.

TABLE I

METAL CHELATES OF *o*-HYDROXYAZOBENZENE

Metal chelated	Color	Metal, %	
		Calcd.[a]	Found
Cu(II)	Brown	14.80	14.55
Ni(II)	Dark green	13.81	14.02
Co(II)	Dark blue	13.87	14.11

[a] Metal contents were calculated from the formula $(C_{12}H_9ON_2)_2M$, where M represented the metal chelated.

Infrared Spectra.—A Perkin–Elmer model 21 double beam spectrophotometer equipped with sodium chloride optics was used for the determination of infrared spectra, and samples were run both as Nujol mulls and as potassium bromide disks. For all the samples, these procedures gave almost identical spectra.

Results and Discussion

The significant absorption bands of these compounds below 1700 cm.$^{-1}$ are shown in Table II, along with assignments to group vibrations where possible.

The only absorption band observed in the 3300 cm.$^{-1}$ region is one due to the characteristic aromatic C–H stretching vibration at 3030 cm.$^{-1}$. This band is stable in position as well as in intensity when one goes from the ligand to the metal che-

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(1) K. Ueno, THIS JOURNAL, **79**, in press (1957).

(2) E. Bamberger, *Ber.*, **33**, 3191 (1900).

(3) P. J. McCarthy, R. J. Hovey, K. Ueno and A. E. Martell, THIS JOURNAL, **77**, 5820 (1955).

TABLE II

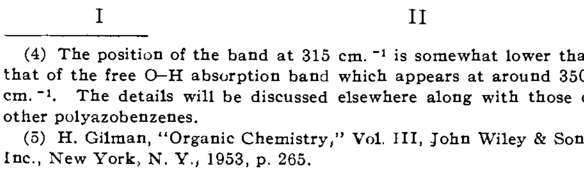
INFRARED ABSORPTION SPECTRA OF *o*-HYDROXYAZOBENZENE AND ITS METAL CHELATES

	o-Hydroxyazobenzene				
		Metal chelates			
Azobenzene	Ligand	Cu(II)	Ni(II)	Co(II)	Assignments
	1610s				C=O of H-bonded ring
1575m	1596s	1602s	1600s	1603s	Phenyl
		1540m	1535w	1531w	C=O of metal chelate ring
1485s	1490s	1490w	1490w		Phenyl
	1471s	1474s	1473s	1475s	Phenyl
1455s	1455s	1460s	1460s	1456s	
1395w	1418s	1400s	1396s	1390s	N=N
	1363m	1341w	1352w	1358w	
	1320w	1330m	1329s	1330s	
1298s	1305w	1296s	1300m	1304m	
	1283s				C–O–H bending of H-bonded ring
	1272s				
	1235w	1252s	1260m	1253w	
1220m	1214m	1212w	1220w	1215w	Phenyl
	1182m	1184m	1185w	1180m	
1156m	1157w	1158w	1157w	1150w	Phenyl
1150m	1143m	1145m	1142s	1138s	
	1111m	1120w	1119w	1119w	*o*-Disubst. phenyl
	1106m				
1069s	1067w	1070w	1070w	1075w	Phenyl
	1026w	1020w	1020w	1023w	*o*-Disubst. phenyl
1018m	1016w			1000w	
997m	997w				
981m		945w	952w	947m	
924s	935w	933w		917w	
	912w	907w		900w	
845w	855w	862w	871w	865w	
		838w		842w	
	807m		800w	794m	Phenyl
772s	770s	787w		760s	
	765s	758m	758s	757s	
	750s	755m		751s	
		750m			
	735m	744s	743s	741s	*o*-Disubst. phenyl
684s	675s	684s	688s	690s	Phenyl
		660w	664w	661m	

lates, indicating that it is due purely to the aromatic C–H stretching vibration.

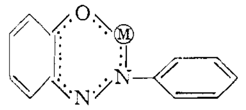
It is striking that no other well-defined band can be found in and around the 3300 cm.$^{-1}$ region on the ligand, since an additional band due to O–H stretching vibration would be expected in this region, as is true of the corresponding *para* derivative, which has a strong band at 3150 cm.$^{-1}$.[4] The absorption due to O–H stretching vibration is known to shift to the lower frequency region and to decrease in intensity as the result of hydrogen bonding. Although a very weak band is found at around 2300 cm.$^{-1}$ on the ligand, it cannot be due to O–H bonding, because the corresponding band with increasing intensity is found on all metal chelates, in which no O–H bonding exists.

There have been many discussions on the structure of *o*-hydroxyazo compounds,[5] since the compounds can have the tautomeric azo (I) and the hydrazone (II) forms. While the chemical and absorption spectrophotometric evidence on the *o*-hydroxyazo compounds in solution favor the hydrazone structure,[6] it has been shown that *o*-hydroxyazobenzene appears in the azo form only, irrespective of the solvent.[7]



I II

In accordance with these observations Hadzi[8] concluded, in his investigation on the *o*-hydroxyazo compounds, that the absorption band due to the O–H stretching vibration of *o*-hydroxyazobenzene was, owing to its intramolecular hydrogen bonding, too weak and too broad to be observed. A broad and rather strong band with a maximum at 1610 cm.$^{-1}$ is observed in the ligand, *i.e.*, *o*-hydroxyazobenzene, but is shifted to lower frequencies in its metal chelate compounds. This absorption probably is due to the C=O stretching vibration of the hydrogen bonded ring system as shown by the formula II. Although the free carbonyl band is expected at around 1700 cm.$^{-1}$, such a bathochromic shift is often observed in hydrogen-bonded ring systems.[9] In the metal chelates, this band is observed at around 1531–1540 cm.$^{-1}$, as the result of involvement of the C=O . . . linkage in the metal chelate ring as shown by formula III.



III

The shift of this band from the original position of the ligand probably is due to the increased mass of the metal attached to the oxygen atom relative to that of the proton and also due to the electronegativity of the metal ions.

Although no quantitative data are available on the stability of the metal chelates of *o*-hydroxyazobenzene, the ease of metal chelate formation and the stability order of metals[10] would indicate that the stability of the metal chelates of *o*-hydroxyazobenzene decreases in the order of Cu > Ni > Co. It may also be noted that the order of decreasing frequency of the band arising from the carbonyl linkage of the metal chelates is parallel to the order of decreasing stability.

Similar shifts of the carbonyl band by metal chelation also were reported for salicylaldehyde and its metal chelates.[9b] However, in these cases, the extent of shift was found to parallel the order of increasing stability of the salicylaldehyde metal chelates. It is not clear why the carbonyl band shifts with increasing stability in one case and with decreasing stability in other case. However, the results of this research indicate that the shift of carbonyl band by metal chelate formation does not result simply from a change of bond order but result from more complicated effects such as the mass of metal ions and the formation of π-orbitals in the

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[4] The position of the band at 315 cm. $^{-1}$ is somewhat lower than that of the free O–H absorption band which appears at around 3500 cm.$^{-1}$. The details will be discussed elsewhere along with those of other polyazobenzenes.

[5] H. Gilman, "Organic Chemistry," Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1953, p. 265.

(6) Fierz-David, *et al.*, *Helv. Chim. Acta*, **29**, 1718 (1946).

(7) R. Kuhn and F. Bär, *Ann.*, **516**, 143 (1935).

(8) D. Hadzi, *J. Chem. Soc.*, 2143 (1956).

(9) (a) R. S. Rassmussen, D. D. Tunicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949); (b) L. J. Bellamy and R. F. Branch, *J. Chem. Soc.*, 4491 (1954).

(10) The stability of complexes of bivalent metal ions generally follows the order of Cu > Ni > Co, irrespective of the nature of the ligands involved, D. P. Mellor and L. Maley, *Nature*, **159**, 370 (1947); **161**, 436 (1948).

chelate ring involving the d-orbitals of the metal ion.

Another considerable change of the spectra resulting from metal chelate formation is found in the bands at 1283 and 1272 cm.$^{-1}$. Although the 1283 cm.$^{-1}$ band appears as a shoulder on the main band at 1272 cm.$^{-1}$, both bands are rather strong and are missing in the metal chelates. Hadzi[8] assigned the band at 1272 cm.$^{-1}$ to the in-the-plane bending mode of the C–O–H group. The fact that the corresponding band is missing in the metal chelates supports this assignment, and either one of these two bands is possibly due to the C–O–H group of the ligand.

No conclusive assignment of absorptions due to the azo linkage has been reported in the literature. Le Fèvre[11] and his co-workers have investigated some 43 aromatic diazonium and azo compounds and found common absorption bands at around 1406 and 1577 cm.$^{-1}$. The main difficulty in the assignment of a frequency to the azo linkage is that the absorption frequency of N=N stretching vibration would overlap with other absorptions such as those of the aromatic ring which are usually of strong intensity.

Of the absorption bands due to the azo linkage, a band corresponding to 1405 cm.$^{-1}$ was found in the polyazobenzenes which we have investigated,[1] and it is believed that this band can be assigned to the azo linkage with certainty. For azobenzene and *o*-hydroxyazobenzene, this absorption band is found at 1395 and 1418 cm.$^{-1}$, respectively. For the metal chelate compounds of *o*-hydroxyazobenzene, this band shifts to lower frequencies as shown in the Table II. The extent of shift is again found to be parallel to the order of decreasing stability of metal chelate compounds.

Acknowledgment.—The author wishes to express his sincere appreciation to Prof. A. E. Martell of Clark University, Worcester, Mass., who so generously carried out the measurement of infrared spectra.

KUMAMOTO-SHI, JAPAN

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(11) R. J. W. Le Fèvre, M. F. O'Dwyer and R. L. Werner, *Australian J. Chem.*, **6**, 341 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF FLORIDA STATE UNIVERSITY]

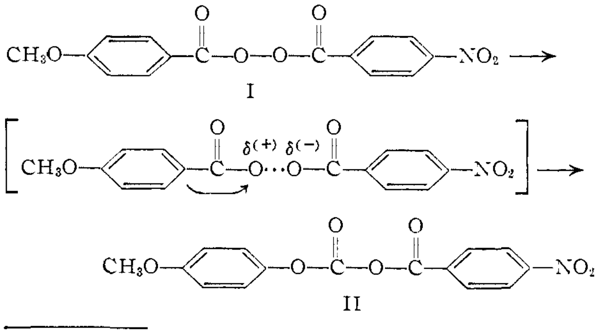
4-Methoxy-3′,5′-dinitrobenzoyl Peroxide[1]

BY JOHN E. LEFFLER AND CONSTANTINE C. PETROPOULOS

RECEIVED DECEMBER 20, 1956

The decomposition of 4-methoxy-3′,5′-dinitrobenzoyl peroxide is accelerated by a shift to a more polar solvent, by acids, and by 1,3,5-trinitrobenzene. Its behavior is compared with that of other diacyl peroxides.

The combined effect of the introduction of a *p*-methoxy and a *p*′-nitro substituent and the use of a polar solvent is sufficient to change the decomposition of benzoyl peroxide from a radical to a non-radical mechanism.[2] The non-radical decomposition is much more sensitive to the polarity of the solvent and can also be recognized from the products. The migration of *p*-methoxyphenyl from carbon to oxygen in the polar decomposition reduces the yield of anisic acid and its esters and in the case of thionyl chloride as a solvent produces the rearrangement or carboxy-inversion product (II).[2,3] The polar decomposition is accelerated by acids as well as by polar solvents.



I

II

Similar experiments have now been done with 4-methoxy-3,′5′-dinitrobenzoyl peroxide. This peroxide is even more sensitive to solvent changes, but the reaction is less clean cut.

The Effects of Substituents and Solvents.—Table I summarizes the combined effects of the various substituents and solvents on the first-order rate constants for the peroxide decomposition; the results are remarkably different from those obtained with symmetrical peroxides. The effects of solvent changes or of symmetrical *meta* or *para* substitution on the rate of homolysis of benzoyl peroxide are usually less than one order of magnitude. For example in acetophenone at 80° the rate constants range from 1.46×10^{-3} min.$^{-1}$ for bis-(*p*-cyanobenzoyl) peroxide to 9.32×10^{-3} min.$^{-1}$ for bis-(*p*-methoxybenzoyl) peroxide.[4] In the solvents benzene, acetophenone, dioxane and styrene the first-order constants of a given benzoyl peroxide are usually the same within a factor of two.[4–6] Benzoyl peroxide decomposes at the same rate in benzene and in nitrobenzene.[7] A drastic change in the rate of a diaroyl peroxide decomposition is therefore likely to mean a change in mechanism.

In benzene the 4-methoxy-4′-nitro substitution

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(1) This work was supported by a Frederick Gardner Cottrell grant from the Research Corporation.

(2) J. E. Leffler, THIS JOURNAL, **72**, 67 (1950).

(3) D. B. Denney, *ibid.*, **78**, 590 (1956).

(4) A. T. Blomquist and A. J. Buselli, *ibid.*, **73**, 3883 (1951).

(5) C. G. Swain, W. H. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

(6) W. Cooper, *J. Chem. Soc.*, 3106 (1951).

(7) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).