1-Methyl-4-cyanoformylpyridinium Oximate. An Indicator of Environment in Solutions

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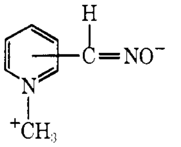
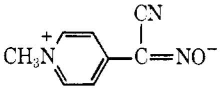
Abstract: The compound 1-methyl-4-cyanoformylpyridinium oximate (CPO) possesses two electronic absorption bands which are measures of solvent polarity. These transitions are attributed to an intramolecular charge transfer (CT) from oximate oxygen to the pyridinium ring and vanish on protonation, metal complexation, or chemical reaction of the oxygen. The solubility, spectral solvent dependence, and zinc and cobalt metal complexes of CPO are described. An outline is given of the factors affecting the choice of CPO as a reagent for probing environment in solution.

The charge-transfer (CT) spectra of numerous substances have been used to correlate solute–solvent interactions with physical and chemical properties of interest. These include rates of reaction, micelle formation, ion pairing, and donor–acceptor excited states.[1] A study of the properties of aldoximates (PA) derived from 2-, 3-, and 4-pyridinium aldoxime methiodides[2] showed that the long wavelength electronic absorption band, which had extinction coefficients of *10,000–20,000*, correlated with Kosower's Z values[3] and was designed as a charge transfer band. Unfortunately, these aldoximates are not very stable when isolated from solution. In the course of studies on CT interactions involving pyridinium compounds, we have found that 1-methyl-4-cyanoformylpyridinium oximate (CPO),



PA



CPO

a very stable compound, has unusual characteristics which render it a useful reagent and probe of solute–solvent interactions. We report here a survey of some of the chemical and physical properties of CPO.

Results and Discussion

Solubility. The solubility of CPO in a number of solvents at 20° is given in Table I. The compound has some solubility in a wide range of solvents from methylene chloride to water. It is insoluble in very nonpolar solvents such as hexane and benzene. There is no single correlation between solubility and either spectroscopic solvent polarity parameters, dielectric constant (D) of the solvent, or any of the usual functions of D.

Electronic Spectra. The first two (longest wavelength) absorption maxima and extinction coefficients of CPO in various solvents are given in Table I. The lowest energy (E_1) band is in the visible with a molar extinction coefficient of about 100. The second band energy (E_2) is in the near uv with a molar extinction coefficient of about 30,000. Both band energies are quite solvent sensitive and correlate linearly with empirical solvent polarity parameters such as Z values[3,4] and $E_{T(30)}$ values.[5,6] The color of the solution is thus an indication of the polarity of the solvent, ranging from blue in methylene chloride and red in acetone to yellow in water. The solid itself is dark red.

Both CT bands are absent in acidic media, in which the oximate oxygen is protonated.[7] In addition, the bands are seen to vanish with reactions (such as alkylation) of the oxygen, providing the anion (*e.g.*, iodide or perchlorate, etc.) has a sufficiently high ionization potential so that the anion to ring intermolecular CT bands do not interfere.

Metal Complexation. As mentioned, alkylation or protonation of CPO leads to a disappearance of the CT bands. It seemed interesting to examine the spectral properties of CPO metal complexes. Accordingly, the metal complexes $M(CPO)_2Cl_2$, where M = Zn or Co, were prepared. Attempts to prepare iron(II) or copper(II) complexes lead to materials of uncertain composition. The cobalt and zinc complexes form cleanly and appear to be air stable and not hygroscopic. Solution spectra could not be obtained since the complexes are not soluble in most solvents. Some dissolution can be effected in dimethylformamide, pyridine, or acetonitrile. However, in all cases ligand dissociation or replacement by solvent occurs. The zinc complex is yellow due to the tailing of uv absorption into the visible as shown by a solid state (Nujol mull) spectrum. As is the case with protonation or alkylation of the oxygen, the CT bands are absent. Infrared mull spectra (Table II) of the metal complexes show that the C=N stretching frequency of the oximate group is raised by 10–15 cm^{-1} and the C≡N frequency by 20–30 cm^{-1}, while the N–O stretching frequency is lowered by about 100 cm^{-1}. These results are consistent with metal ion coordination *via* the oximate oxygen, since complexation should increase the contribution of the primary

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(1) R. A. Mackay, J. R. Landolph, and E. J. Poziomek, *J. Amer. Chem. Soc.*, **93**, 5026 (1971), and references therein.

(2) N. Engelhard and B. Werth, *Tetrahedron Lett.*, 661 (1963).

(3) E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253 (1958).

(4) Energy in kcal mol^{-1} of the peak maximum of the intermolecular CT band of 1-ethyl-4-carbomethoxypyridinium iodide.

(5) C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965).

(6) Energy in kcal mol^{-1} of the peak maximum of the intramolecular CT band of a pyridinium-*N*-phenolbetaine.

(7) The pK_a is reported to be 4.6 (ref 8).

(8) E. J. Poziomek, R. H. Poirier, B. W. Fromm, D. N. Kramer, J. A. Stockinger, and M. D. Pankau, *J. Org. Chem.*, **29**, 217 (1964).

Table I. Solubility and First and Second Charge-Transfer Bands of 1-Methyl-4-cyanoformylpyridinium Oximate in Various Solvents

Solvent	Solubility[a]	E_1[b]	ϵ_1[c]	E_2[b]	ϵ_2[c]	$E_2 - E_1$
Water	140	65.7	0.10	83.8	24	18.1
0.05 M H_2SO_4 (aq)		*d*	*d*	*d*	*d*	
Methanol	9.0	59.6	0.08	78.7	29	19.1
0.05 M H_2SO_4 (MeOH)		*d*	*d*	*d*	*d*	
Ethanol	1.5	57.2	0.09	77.1	30	19.9
Ethyl formate	*e*	*e*	*e*	76.3	*e*	
2-Propanol	0.26	55.1	0.07	75.9	29	20.8
1-Pentanol	0.28	*e*	*e*	75.9	29	
Dimethyl sulfoxide	87	51.3	0.10	75.3	41	24.0
Acetonitrile	7.5	51.0	0.08	74.9	36	23.9
Acetone	2.5	49.5	0.08	73.6	37	24.1
Ethyl acetate	0.12	*e*	*e*	72.5	21	
Methylene chloride	0.74	48.8	0.06	71.9	30	23.1

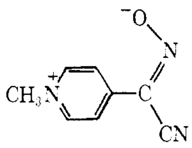
[a] Solubility at 20° in $M \times 10^3$. [b] Band energy in kcal mol^{-1} ($\pm$0.2 kcal mol^{-1}). [c] Extinction coefficient in M^{-1} cm^{-1} $\times 10^3$. [d] Absent. [e] Solubility too low for measurement.

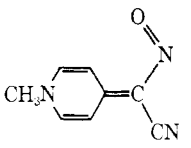
resonance form A relative to the resonance forms B and C. The zinc complex is presumably tetrahedral. The electronic spectrum of the solid cobalt complex is consistent with tetrahedral coordination, the visible absorption occurring about 16,000 cm^{-1}.

Table II. Infrared Stretching Frequencies of Zn(II) and Co(II) Chloride Complexes of CPO[a]

Compound	C≡N[b]	C=N[c]	N-O[d]
CPO	2185	1620	1265, 1250
$Zn(CPO)_2Cl_2$	2215	1635	1173, 1157
$Co(CPO)_2Cl_2$	2205	1630	1155, 1145

[a] Frequency in cm^{-1}. [b] $\pm$10 cm^{-1}. [c] $\pm$3 cm^{-1} (C=N of oximate group). [d] $\pm$3 cm^{-1}.


A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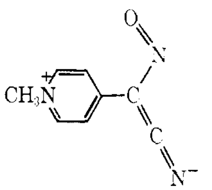
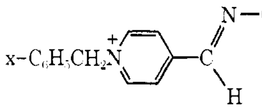

C

Nature of the Transitions. The magnitude and direction of the solvent dependence of E_1 and E_2 and their correlation with other inter- and intramolecular CT band energies suggest that the transitions are of a similar nature. The disappearance of the bands upon protonation, alkylation, or complexation with metal ion indicates that the oxygen atom is involved. There is considerable delocalization in this system, and a molecular orbital treatment of the entire molecule is needed to adequately describe the transitions. Nonetheless, the infrared spectra indicate that A is the primary resonance form, and as a model we can consider that a CT transition involves promotion of an electron from a molecular orbital largely localized on oxygen to an antibonding π molecular orbital (π^*) concentrated largely on the pyridinium ring. In this regard we may note that there will be some overlap of one p orbital on oxygen with the C-3 p π orbital on the ring. This "through space" interaction between oxygen and the pyridinium π system is possible since 4-pyridineglyoxylonitrile oxime (mp 276–278°) and its alkylated derivatives have been assigned configuration with the oxime group cis to pyridinium ring (A).[9,10] This is consistent with the large spectral solvent shifts of CPO which indicate a significant change in direction of the electric dipole moment between ground and excited states. On the other hand 1-(para-substituted benzyl) oximate derivatives (D) of *syn*-isonicotinaldehyde oxime show little shift of the lowest band energy between methylene chloride and methyl formate.[11]


D

The question now arises as to why two CT bands are observed for pyridinium oximates. One possibility is that an electron is being promoted to either the first or second vacant molecular orbital (MO) on the ring. Evidence has been presented which indicates that this is the explanation for the CT spectra of pyridinium iodides.[1] In the case of 4-substituted 1-alkylpyridinium iodides in CH_2Cl_2, the separation between the two CT bands (ΔE) is about 28 kcal mol^{-1}. For CPO, ΔE in CH_2Cl_2 is 23.1 kcal mol^{-1}. Also, both bands were of comparable intensity in the iodide salts (about 1000 M^{-1} cm^{-1}) while in CPO the second band is about 300 times more intense. It therefore seems probable in this case that both transitions involve electron transfer into the same orbital, namely the lowest empty (Py π^*) orbital on the ring.

If, for both transitions, electron donation occurs from the same orbital on oxygen, then a second possibility is that the two CT bands are due to triplet and singlet excited states arising from promotion of the electron to the first vacant (Py π^*) MO. The ΔE of 1 eV (23 kcal mol^{-1}) is on the order of the energy difference between a singlet and triplet state. Since the ground state is a singlet, the first (lower energy) band should be several hundred times less intense than the second band, as observed. However, the absolute value of the extinction coefficient for a singlet–triplet transition is at least a hundred times lower than ϵ_1 and extensive spin–orbit coupling is unlikely.

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(9) B. C. Tyson, Jr., E. J. Poziomek, and E. R. Danielson, *J. Org. Chem.*, **34**, 3635 (1969).

(10) B. C. Tyson, Jr., Ph.D. Thesis, University of Delaware, June 1969.

(11) D. W. Reger and E. J. Poziomek, unpublished results.

By the process of elimination, the third and most likely possibility is that donation occurs from two different oxygen orbitals. There are three "nonbonding" electron pairs on oxygen, one pair in the 2s orbital and two pairs in 2p orbitals (neglecting hybridization). The nonbonding s orbital (ns_O) is lowest in energy. One of the p orbitals lies in the plane of the molecule (np_O), while the other is perpendicular to the molecular plane ($np\pi_O$). As mentioned above, the $np\pi_O$ orbital is largely localized on oxygen but does overlap with the π MO's of both the aldoximate C=N and the ring, and should thus be lower in energy than the np_O orbital. The two CT transitions may then be described as

$$np_O \xrightarrow{E_1} \text{Py } \pi^*$$

and

$$np\pi_O \xrightarrow{E_2} \text{Py } \pi^*$$

The band intensities are also explained by this model since the np_O–Py π^* overlap is small compared with the $np\pi_O$–Py π^* overlap, similar to the situation for localized $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. In contrast to the latter localized transitions, both bands are shifted to higher energy with increasing solvent polarity. The solvent sensitivity of the second (higher energy) band is less due to the partial π character of the donor orbital. The observation of an emission band arising from excitation of the short wavelength band, but not from the long wavelength band, would help to support this assignment. However, no emission was observed between room and liquid nitrogen temperatures in a variety of solvents. Unfortunately, our instrument was limited to a long wavelength maximum of 700 nm, and anomalously large Stokes shifts (10,000–20,000 cm^{-1}) have been reported for fluorescence from excitation of the CT bands of pyridinium salts.[12]

Factors Affecting the Choice of CPO as a Reagent for Probing Environment in Solutions. CPO is easily prepared from 4-pyridineglyoxylonitrile oxime which in turn can be purchased or synthesized from isonicotinaldehyde oxime.[8,13]

CPO is very stable and has been stored for years under ambient laboratory conditions without decomposition.

A choice of CPO concentrations for probing solvent polarity is available since CPO possesses both weak and strong CT bands whose energies correlate linearly with empirical solvent polarity parameters.

Modification of solubility properties can be accomplished easily by preparing CPO derivatives with appropriate pyridinium N-substituents.

The CT bands of CPO are due to intramolecular effects and follow Beer's law (10^{-6} *M* to limit of solubility).

CPO reacts easily with a variety of alkylating, acylating, and sulfonylating chemicals[8] with a loss of the CT bands. Analytical methods for these materials on the basis of resulting CT band intensity could be developed.[14]

CPO reacts with certain metal ions to give insoluble complexes.

Experimental Section

1-Methyl-4-cyanoformylpyridinium Oximate. This compound was prepared according to the method of Poziomek and coworkers.[8]

Zinc(II) and Cobalt(II) Chlorides of CPO. A stoichiometric excess of the hydrated metal chloride was dissolved in ethanol and filtered to remove any cloudiness. The ligand (CPO) was added and the suspension was stirred for about 1 day. The metal complex was filtered off, washed with ethanol and ether, and dried *in vacuo*.

Anal. Calcd for $Zn(C_8H_7N_3O)_2Cl_2$: C, 41.9; H, 3.1; N, 18.3; O, 7.0; Cl, 15.5; Zn, 14.2. Found: C, 41.9; H, 2.9; N, 18.5; O, 6.7; Cl, 15.3; Zn, 14.2.

Anal. Calcd for $Co(C_8H_7N_3O)_2Cl_2 \cdot 0.14CoCl_2$: C, 40.9; H, 3.0; N, 17.9; Co, 14.3. Found: C, 41.1; H, 3.1; N, 17.6; Co, 14.2. No attempt was made to extract the excess $CoCl_2$.

Physical Measurements. The electronic spectra were obtained on a Cary 14 spectrophotometer. Liquid samples were run in 1-cm quartz cells with the solvent as reference. Solid samples were run as Nujol mulls on Whatman No. 1 filter paper with Nujol as reference. Solubilities were determined by dissolving the solid hot and letting it equilibrate to 20° in a constant temperature bath. Aliquots were then withdrawn, appropriate dilutions made, and the concentrations determined spectrophotometrically on a Cary 14 spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer 621 spectrophotometer, the samples being run as Nujol mulls between KRS-5 plates.

Analyses. Elemental analyses were performed by the Analytical Research Department, Chemical Research Laboratory, Edgewood Arsenal.

Acknowledgment. Some of the spectral measurements were made by one of the authors (E. J. Poziomek) during the course of a Secretary of the Army Research and Study Fellowship at the State University of New York at Stony Brook.

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[12] G. Briegleb, J. Trenscseni, and W. Herre, *Chem. Phys. Lett.*, 3, 146 (1969).

[13] E. J. Poziomek and A. R. Melvin, *J. Org. Chem.*, **26**, 3769 (1961).

[14] An analytical method for iodide based on the intermolecular CT absorbance of 1-methyl-4-cyanopyridinium iodide has been reported: E. J. Poziomek and D. W. Reger, *Anal. Chim. Acta*, **58**, 459 (1972).