# Hydrogen Bonding in β-Nitro Alcohols. III. Pyridine Complexes[1,2]

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## Abstract

β-Nitro alcohols form stable 1:1 complexes with pyridine, examples of which have been prepared. In solvents such as dichloromethane and carbon tetrachloride these complexes partially dissociate into their components. The dissociation constants for these equilibria have been determined by infrared methods and may be used as a measure of the strength of the complex hydrogen bond. The dissociation constants decrease with increasing number of β-nitro groups. Some reactions of the pyridine complexes are described.

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## Introduction

Complexes between primary alcohols and tertiary amines have been investigated previously.[3-7] The dissociation energies[3] and association constants in carbon tetrachloride[4] have been determined for

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(3)  M. Tsuboi, J. Chem. Soc. Japan, Pure Chem. Sect., 72, 146 (1951).

(4)  G. M. Barrow, J. Am. Chem. Soc., 76, 5247 (1954).

(5)  V. I. Malyshev, Compt. rend. acad. sci. U.S.S.R., 24, 676 (1939).

(6)  S. Hatem and S. Valladas-Dubois, Compt. rend., 228, 75 (1949).

(7)  S. Hatem and S. Valladas-Dubois, Bull. soc. chim. France, 604 (1949).

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selected pairs. The complexes usually show bonded hydroxyl absorption in the infrared at 3630-3406 cm$^{-1}$,[4,5] which has been attributed to hydrogen bonds.[5] Evidence from ultraviolet absorption spectra indicates that the combination occurs in the ratio of one mole of alcohol per mole of amine,[6] i.e., the complexes may be written as ROH:NR$_3$. The present investigation is concerned with the preparation and properties of similar complexes with β-nitro alcohols which have not been described in the literature.

## Experimental

Materials. The alcohols used in this investigation have been described in the preceding paper.[1] Analytical reagent grade pyridine, carbon tetrachloride, and dichloromethane were used for making up the solutions.

Measurements. Pyridine complexes were prepared freshly, immediately before use, by mixing weighed amounts of alcohol and pyridine. Infrared absorption spectra of the liquid complexes were determined in capillary cells, those of the complex solutions in matched sodium chloride cells of 0.1 and 0.05 cm. length against pyridine solutions of the same concentration in the reference beam. Details of the measuring technique are given in paper II.[1] The properties of the complexes are listed in Table I.

Reactions of the pyridine complexes. The reactions of the complexes with acid chlorides took place in dichloromethane, in which both the pyridine complexes with nitro alcohols and those with acid chlorides are soluble. The experimental conditions are given for one example. Other compounds were prepared similarly.

2,2-Dinitropropyl ethyl carbonate. Ethyl chlorocarbonate (1.08 g., 0.01 mole) was added slowly with stirring to a solution of 2,2-dinitropropanol (1.50 g., 0.01 mole) and pyridine (0.79 g., 0.01 mole) in dichloromethane (10 ml.). The mixture was allowed to stand at room temperature for 16 hrs. and refluxed 1 hr. The infrared spectrum showed complete reaction. The solution was washed twice with 1% hydrochloric acid and three times with water, dried, and evaporated under reduced pressure to give 1.92 g. (86%) of pale yellow oil. One distillation from a molecular still gave colorless ester, b.p. 90° (0.15 mm.), $n_D^{25}$ 1.4418, $\lambda_{C=O}^{liq}$ 5.67, $\lambda_{NO_2}^{liq}$ 6.33, 7.55, $\lambda_{C-O}^{liq}$ 7.96$\mu$.

Anal. Calcd. for $C_6H_{10}N_2O_7$: C, 32.44; H, 4.53; N, 12.61. Found: C, 31.81; H, 4.98; N, 12.61, 12.59.

Ethoxycarbonylpyridinium chloride. A colorless hygroscopic precipitate was formed when pure pyridine (0.79 g., 0.01 mole) was

## TABLE I

### PYRIDINE COMPLEXES OF β-NITRO ALCOHOLS

| Alcohol | $n_D^{25}$ [a] | $\lambda_{OHN}$ [b] | $\lambda_{as-NO_2}$ | $\lambda_{s-NO_2}$ | $\lambda_{C-O}$ | Color |
|---|---|---|---|---|---|---|
| $CMe_3CH_2OH$ | 1.4491 | 3.02m | ----- | ------ | 9.47m | colorless |
| $CMe_2(NO_2)CH_2OH$ | 1.4697 | 3.13m | 6.48s | 7.41m | 9.36m | colorless |
| $CMe(NO_2)_2CH_2OH$ | 1.4786 | 3.22m | 6.36s | 7.50m | 9.27m | pale yellow |
| | ------ | 3.18m[c] | 6.38s | 7.51m | 9.24m | pale yellow |
| $C(NO_2)_3CH_2OH$ | 1.5450 | 3.25m | 6.25s | 7.67m | 9.13m[d] | yellow |
| $CH(NO_2)(CH_2OH)_2$ | 1.4961 | 3.16m | 6.42s | 7.36m | 9.38m | colorless |
| $CMe(NO_2)(CH_2OH)_2$ | 1.4970 | 3.14m | 6.48s | 7.40m | 9.39m | colorless |
| $C(NO_2)_2(CH_2OH)_2$ | 1.4988 | 3.23m | 6.36s | 7.52m | 9.26m[d] | pale yellow |
| | ------ | 3.18m[c] | 6.38s | 7.52m | 9.27m[d] | pale yellow |
| $C(NO_2)(CH_2OH)_3$ | 1.5091 | 3.14m | 6.47s | 7.40m | 9.38m | colorless |

[a] Refractive index of the pure complexes.

[b] Infrared absorption bands in liquid films of the pure complexes, except as noted.

[c] Infrared absorption bands in 0.1 M. pyridine solutions of the alcohols.

[d] A doublet occurs in these cases and one band of the doublet is assigned to C-O stretching on the basis of analogy with the alcohols.

added to a solution of ethyl chlorocarbonate (1.08 g., 0.01 mole)
in 10 ml. of carbon tetrachloride. It was filtered with suction,
washed with carbon tetrachloride, and dried, yield, 1.62 g. (87%),
m.p. 46° (dec.).

Anal. Calcd. for $C_8H_{10}ClNO_2$: N, 7.47. Found N, 7.33.

## Results

β-Nitro alcohols react with one mole of pyridine per β-hydroxyl
group to give stable complexes which exhibit essentially the same
$NO_2$-stretching bands (Table I) as the alcohols themselves.[1,8] Even

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(8) H. E. Ungnade and L. W. Kissinger, Tetrahedron, 00, 000 (1963).

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the C-O stretching frequencies are not appreciably altered by complex
formation, the major change occurring in the OH-stretching region.
While the free β-nitro alcohols have an OH-stretching band near 2.8μ
in solutions and near 3.0μ in potassium bromide,[8] their pyridine
complexes have broad absorption bands at 3.1-3.25μ (Table I)
which are characteristic for the complexes and assigned to bonded
hydroxyl.

In dilute solutions in carbon tetrachloride and dichloromethane the
pyridine complexes dissociate at room temperature to free nitro
alcohols, as evidenced by the appearance of an OH-stretching band
near 2.78μ, and free pyridine. The dissociation equilibria have
been investigated for one nitro alcohol in dichloromethane and for four
alcohols with similar structures in carbon tetrachloride.

The dissociation of dilute solutions of the pyridine complexes in carbon tetrachloride can be suppressed by using an excess of pyridine, as judged by the disappearance of the monomer hydroxyl band, more pyridine being required for the weaker complexes (Table II). Thus qualitatively the amount of pyridine required to prevent dissociation is a measure of the complex bond strength. In solutions with such an excess of pyridine Beer's law holds and one can determine apparent molar absorptivities for bonded hydroxyls.

Solutions of equimolar amounts of alcohol and pyridine in carbon tetrachloride have both monomer and complex bands. Their intensities may be used to determine the concentrations of free alcohol and complex by assuming that a change in the amount of pyridine does not change the molar absorptivities of alcohol and complex bands appreciably. Plots of these data as a function of concentration are given in Fig. 1 and 2.[9]

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(9) The molar absorptivities for the alcohol bands are taken from plots of concentration against absorbance of the pure alcohols in carbon tetrachloride, those of the complex bands from carbon tetrachloride solutions with sufficient pyridine to suppress dissociation (cf Table II).

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Dissociation constants have been calculated from these values and plotted as a function of concentration. For infinitely dilute solutions the constants for the two bands are identical for the strong
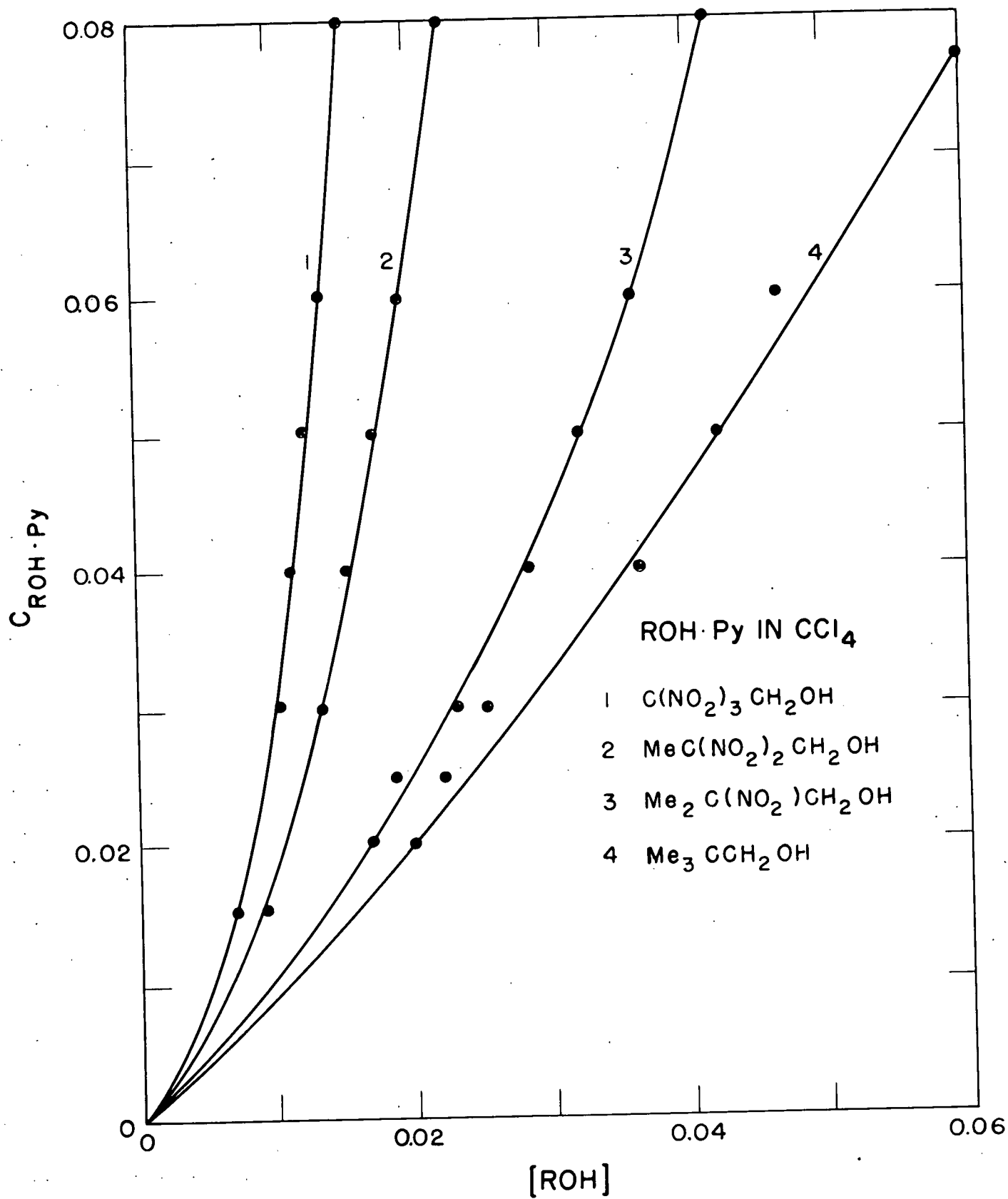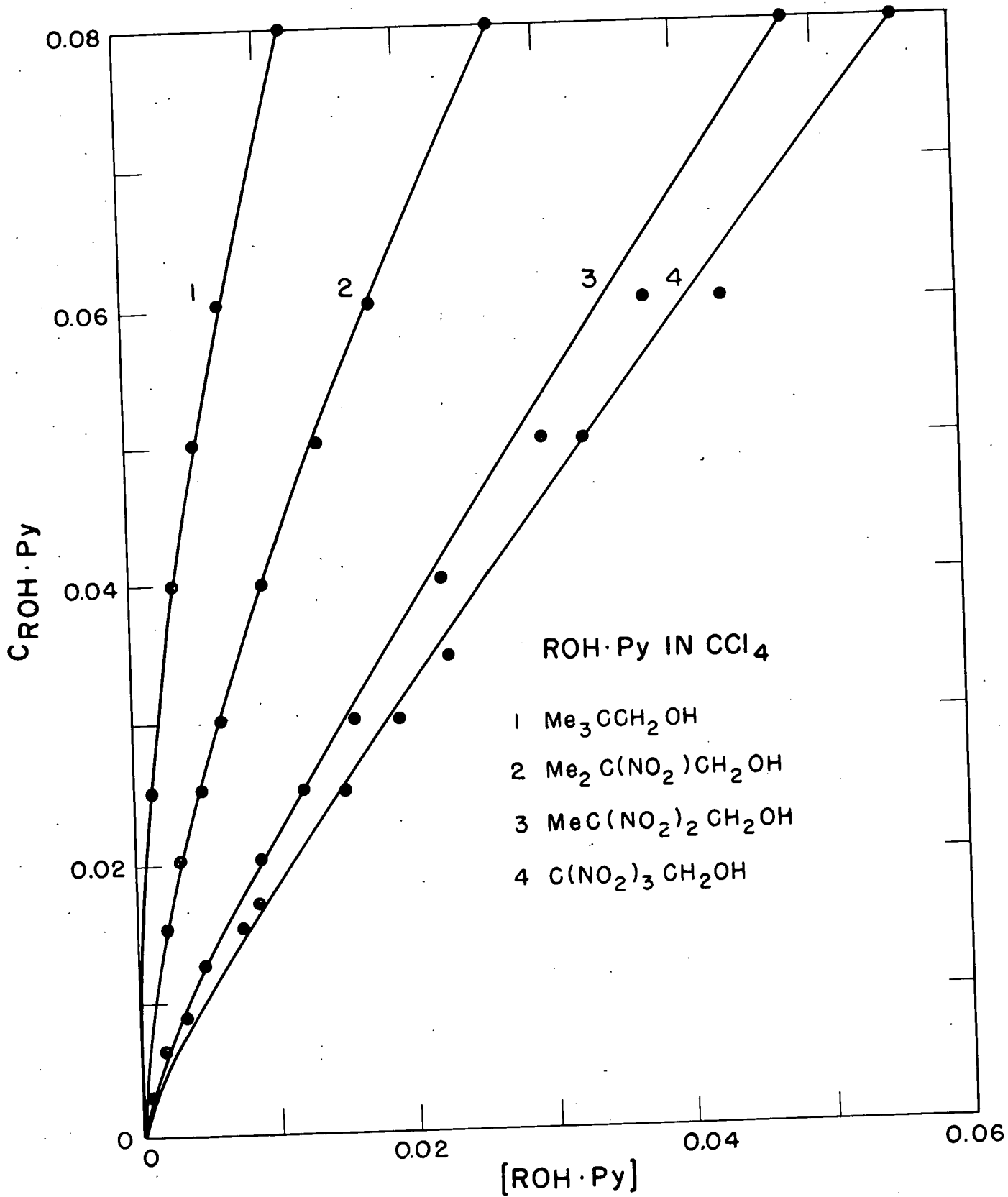
Fig. 1

Fig. 2

## TABLE II

### DISSOCIATION CONSTANTS OF ALCOHOL-PYRIDINE COMPLEXES IN CARBON TETRACHLORIDE

| Alcohol | Moles Py [a] | $\lambda_{OHN}$ | Moles Py [b] | $e^c$ | $K_D^c$ | $e^d$ | $K_D^{'d}$ |
|---|---|---|---|---|---|---|---|
| Neopentyl | 500[e] | 3.02 | 10 | 118 | 0.45 | 125 | 0.20 |
| 2-Methyl-2-nitro-propanol | 50 | 3.11 | 10 | 106 | 0.082 | 110 | 0.082 |
| 2,2-Dinitropropanol | 10 | 3.18 | 5 | 91 | 0.016[f] | 94 | 0.013 |
| Trinitroethanol | 5 | 3.22 | 2 | 76 | 0.0065 | 73 | 0.0065 |

[a] Amount of pyridine per mole of alcohol required to suppress dissociation.

[b] Amount of pyridine per mole of alcohol used for the determination of $K_D$.

[c] Molar absorptivities and dissociation constants from complexes with excess of pyridine.

[d] Molar absorptivities determined with the excess of pyridine given under (a), dissociation constants from 1:1 complexes at infinite dilution:

$$K_D' = \frac{[ROH]^2}{C_{ROH \cdot Py} - [ROH]}$$

[e] Approximate number of moles of pyridine per mole of alcohol without carbon tetrachloride.

[f] In dichloromethane the corresponding dissociation constant (determined with 10 moles of pyridine) was 0.086 and the molar absorptivity of the bonded hydroxyl was 77.

complexes, e.g. those with dinitropropanol and trinitroethanol. For weaker complexes the agreement is not as good.

More precise dissociation constants have been determined in solutions of complexes containing an excess of pyridine but not sufficient to suppress dissociation. Since the complexes in this case are much stronger than others investigated previously, relatively small excesses of base are sufficient to inhibit dissociation. Thus it is not feasible to use the simplified equations which have been employed previously.[10] Sufficient excess of base to neglect the complex

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(10) R. E. Merrifield and W. D. Phillips, J. Am. Chem. Soc., 80, 2778 (1958).

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concentration in the expression $[Py] - C_{ROH \cdot Py}$ could be used only in the case of 2-methyl-2-nitropropanol. The plot of $\dfrac{[ROH] \ell}{A}$ against

$\dfrac{1}{[Py]}$ for this alcohol was linear and the complex therefore 1:1, as in the case of simple alcohols. For the determination of the association constants K for the alcohol-pyridine equilibria
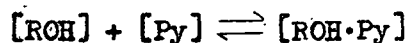
$$[ROH] + [Py] \rightleftharpoons [ROH \cdot Py]$$

the mixtures were carefully analyzed for the complex band at 3.02-3.24μ. Concentrations of alcohol and pyridine were derived from analytical concentrations, i.e. $[ROH] = C_{ROH} - [ROH \cdot Py]$ and $[Py] = C_{Py} - [ROH \cdot Py]$, and the absorbance of the complex from molar absorptivity $\epsilon_c$, cell length $\ell$, and molar concentration of the complex:

$A_{ROH \cdot Py} = [ROH \cdot Py] \epsilon_c \ell$. In terms of concentrations of starting materials, this equation becomes:

$$A_{ROH \cdot Py} = K(C_{ROH} - [ROH \cdot Py])(C_{Py} - [ROH \cdot Py])\epsilon_c \ell$$

$$= KC_{ROH}C_{Py}\epsilon_c \ell - [ROH \cdot Py]K(C_{ROH} + C_{Py} - [ROH \cdot Py])\epsilon_c \ell$$

For simplification

$$\frac{1}{C_{ROH} + C_{Py} - [ROH \cdot Py]} = Y \quad \text{and} \quad \frac{C_{ROH} C_{Py} \ell}{C_{ROH} + C_{Py} - [ROH \cdot Py]} = X;$$

thus,

$$Y \cdot A_{ROH \cdot Py} = XK\epsilon_c - KA_{ROH \cdot Py}$$

$$A_{ROH \cdot Py}(Y + K) = K\epsilon_c X$$

or,

$$\frac{X}{A_{ROH \cdot Py}} = \frac{Y + K}{K\epsilon_c} = Y\frac{1}{K\epsilon_c} + \frac{1}{\epsilon_c}$$

When $\dfrac{X}{A_{ROH \cdot Py}}$ was plotted against Y for a number of solutions, the plots were linear, the intercepts were $\dfrac{1}{\epsilon_c}$, and $\dfrac{1}{K}$ was found from $\epsilon_c$ times the slope of the lines. The data were calculated by using an assumed K value, equivalent to 90% association, plotting Y against $\dfrac{X}{A_{ROH \cdot Py}}$, and determining $\epsilon_c$ and a new K. The found constant was used to determine the concentration of complex, i.e.:

$$[ROH \cdot Py] = \frac{(C_{ROH} + C_{Py} + \frac{1}{K}) \pm \sqrt{(C_{ROH} + C_{Py} + \frac{1}{K})^2 - 4 C_{ROH}C_{Py}}}{2}.$$

Using the new complex concentration, new values for Y and $\dfrac{X}{A_{ROH \cdot Py}}$ were

calculated and plotted and the constant redetermined until no

further change occurred. The molar absorptivities and dissociation

constants $K_D = \frac{1}{K}$ are listed in Table II. Figure 3 gives the plot

of Y against $\frac{X}{A_{ROH \cdot Py}}$ for dinitropropanol·10pyridine as an illustra-

tion of the method.

## Discussion

β-Nitro alcohols may be expected to react with bases such as

pyridine by complexing through the alcoholic hydroxyl,[3-7] the nitro

group,[11] or both, or by a cleavage reaction yielding formaldehyde,

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(11) H. E. Ungnade, E. D. Loughran, and L. W. Kissinger, J. Phys.

Chem., 64, 1410 (1960).

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such as occurs with aqueous bases.[12] Infrared absorption spectra

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(12) T. N. Hall, Abstracts of the papers of the symposium on

nitro aliphatic chemistry, May 25 and 26, 1961, Purdue University,

W. Lafayette, Indiana, page 8.

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indicate that a reversal of the Henry reaction of this sort does not

occur with pyridine in anhydrous non-polar solvents or without solvents.

The experimental evidence has established that the main reaction is the

formation of a relatively strong 1:1 complex between β-nitro alcohol

hydroxyl and pyridine, which increases in strength with the number of

DINITROPROPANOL·
10 PYRIDINE IN $CH_2Cl_2$

$\frac{1}{\epsilon} = 0.013$ ; $\epsilon = 77$

$\frac{1}{K} = 77 \times \frac{0.0056}{5}$

$\frac{1}{K} = 0.086$
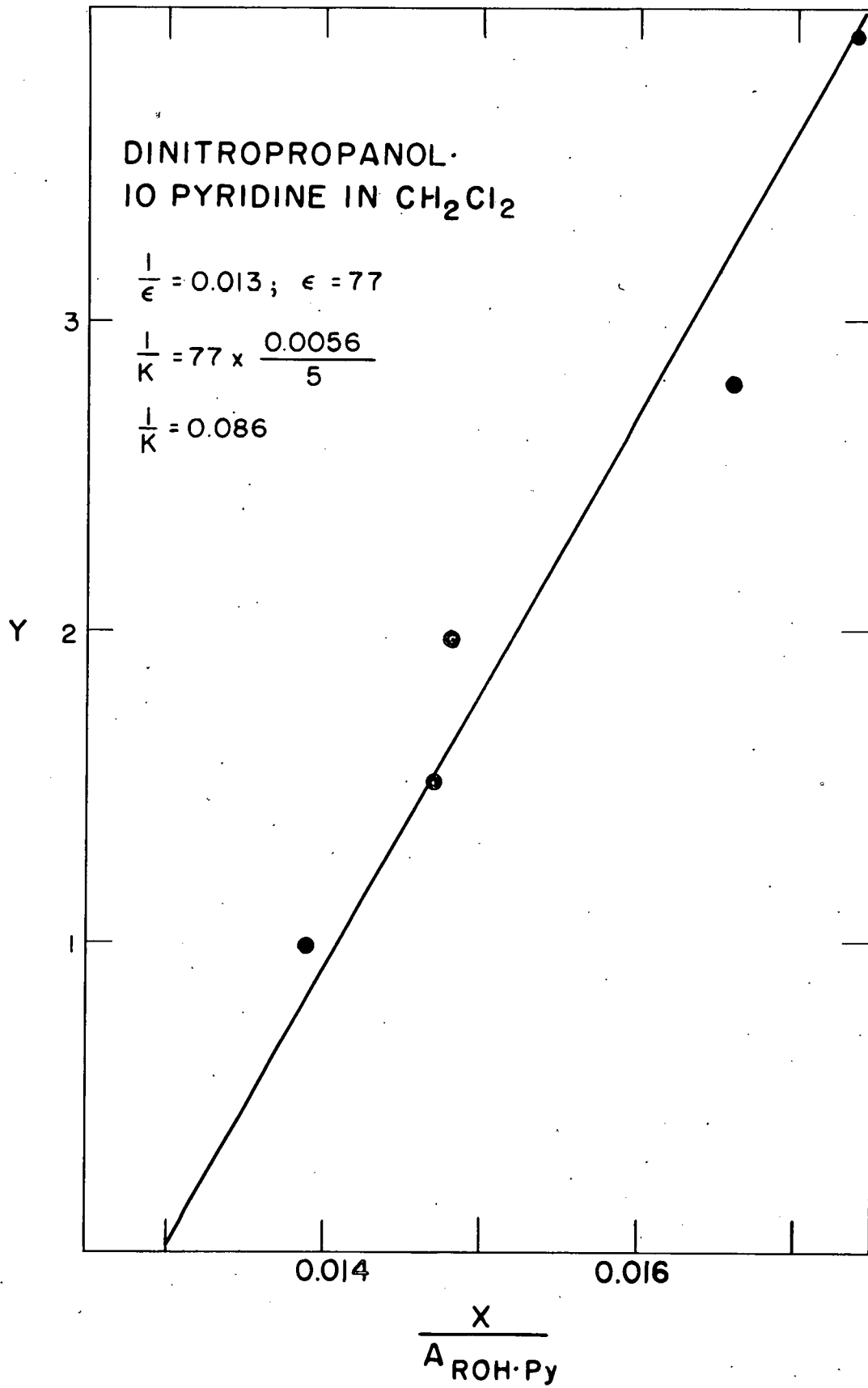
Fig. 3

β-nitro groups, and that other interactions may be neglected, particularly with the stronger complexes.

Further investigations have established that pyridine complexes of β-nitro alcohols do not react with alkyl and allyl halides. It has been shown previously, however, that β-nitro alcohols undergo smooth reactions with acyl halides in the presence of pyridine in solvents such as dichloromethane,[13] provided that the reaction conditions are properly

(13) Numerous esters of β-nitro and dinitro alcohols and diols have been prepared by this method in these laboratories (L. W. Kissinger, T. M. Benziger, H. E. Ungnade, and R. K. Rohwer, J. Org. Chem., in press).

chosen. High yields of esters can be obtained by a modification of this method even from highly acidic β-nitro alcohols, such as trinitroethanol, 2-chloro-, and 2-bromo-2,2-dinitroethanol.[14,15] While pyridine has been used extensively in esterification reactions of simple

(14) H. E. Ungnade and L. W. Kissinger, J. Org. Chem., 00, 000 (1963).

(15) Most previous methods of esterification of such alcohols have employed acidic conditions, perhaps because of anticipated side reactions with pyridine. See: L. W. Kissinger, M. Schwartz, and W. E. McQuistion, J. Org. Chem., 26, 5203 (1961); H. Feuer, G. B. Bachman, and J. P. Kispersky, J. Am. Chem. Soc., 73, 1360 (1951); H. Feuer and W. A. Swarts, J. Org. Chem., 27, 1455 (1962); M. B. Frankel, J. Org. Chem., 23, 813 (1958).

alcohols,[16] it was believed that the beneficial effect was due to its

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(16) These include one example of a mononitro alcohol which was esterified in excess pyridine [M. S. Heller and R. A. Smiley, J. Org. Chem., 23, 771 (1958)].

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solvent action on alcohol and acid chloride and the removal of the formed acid. The mechanism for the reaction is written with an acylpyridinium salt intermediate.[17] The high yields in the case of

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(17) M. L. Bender, Chem. Rev., 60, 77 (1960).

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the more acidic β-nitro alcohols, which form strong pyridine complexes, make it apparent that pyridine must be more directly involved in these esterification reactions.

The reaction therefore has been examined in detail for 2,2-dinitro-propanol, ethyl chlorocarbonate, and pyridine in dichloromethane. A 1M solution of these reactants gives a high yield of ester as the only product after 1-2 hours of refluxing. Infrared absorption spectra have been determined for the components singly and in pairs in di-chloromethane. The results show that there is no interaction between ethyl chlorocarbonate and dinitropropanol. Both infrared absorption bands and ultraviolet curve ($\lambda_{max}^{CH_2Cl_2}$ 278, $\varepsilon = 59$) are identical in shape and intensities with those of the pure constituents. Ethyl chlorocarbonate and other acid chlorides react with pyridine to give

acylpyridinium chlorides, which can be precipitated in solvents such as ether, benzene, chloroform, carbon tetrachloride, or ligroin.[18]

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(18) W. M. Dehn, J. Am. Chem. Soc., 34, 1408 (1912); M. Dennstedt and J. Zimmermann, Ber., 19, 75 (1886); J. L. Hales, J. I. Jones, and W. Kynaston, J. Chem. Soc., 623 (1957).

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Pure solid ethoxycarbonylpyridinium chloride has been prepared in this fashion. Its infrared spectrum has characteristic bands, quite different from those of the starting materials (Table III). In dichloromethane solution, however, the bands of chlorocarbonate and pyridine reappear and become stronger with increasing dilution, i.e., the salt dissociates in this solvent:
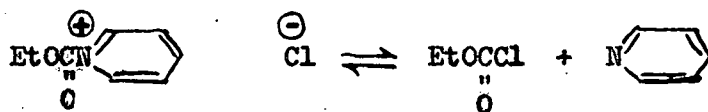


The extent of the dissociation is quite large (75% in a 0.1 M dichloromethane solution at 25°), corresponding to a dissociation constant of 0.23. By comparison the pyridine complexes of dinitro and trinitro alcohols dissociate to a smaller degree ($K_D^{25°}$ = 0.086 for dinitropropanol in dichloromethane). In a mixture of the three components the acylpyridinium salts may therefore be unimportant.

The spectrum of the homogeneous 0.1 M solution (each) of dinitropropanol, ethyl chlorocarbonate, and pyridine in dichloromethane at 25° changes with time, i.e., there is a measurable amount of reaction. This reaction could be minimized by mixing the components

## TABLE III

### INFRARED ABSORPTION BANDS FOR 2,2-DINITROPROPANOL, PYRIDINE, AND ETHYL CHLOROCARBONATE IN DICHLOROMETHANE

| Compound | Solvent | $\lambda_{OH}$ | $\lambda_{CHN}$ | $\lambda_{C=O}$ | $\lambda_{as-NO_2}$ | $\lambda_{s-NO_2}$ | $\lambda_{C-O}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| ROH[a] | $CH_2Cl_2$ | 2.78m | | | 6.34s | 7.54m | | | | 9.30m |
| ROH·R'COCl | $CH_2Cl_2$ | 2.78m | | 5.61s | 6.34s | 7.54m | | 8.55m | 8.75m | 9.30w |
| R'COCl | $CH_2Cl_2$ | | | 5.61s | | | | 8.55m | 8.75m | |
| ROH·Py | $CH_2Cl_2$ | 2.78m | 3.25m | | 6.35s | 7.54m | | | | 9.27m |
| R'COPy$^+$ Cl$^-$ | $CH_2Cl_2$ | | | 5.49m 5.62m | | | 8.02m[c] | 8.55m | 8.75m | |
| | KBr | | | 5.54s | | | 8.05s | | | |
| ROH·Py·R'COCl | $CH_2Cl_2$ | 2.78w | 3.20m | 5.48m 5.62m | 6.34s | 7.54m | 7.98s[c] | b | | 9.30m |
| R'COOR | $CH_2Cl_2$ | | | 5.67s | 6.34s | 7.55m | 8.07m[c] | | | |
| | Liq. | | | 5.67s | 6.35s | 7.55m | 8.00s | | | |

[a] ROH = 2,2-dinitropropanol, R'COCl = EtOCOCl, Py = pyridine

[b] Weak absorption for free R'COCl was observed at 8.5-8.8μ.

[c] The exact values are uncertain because of adjacent solvent absorption.

at 0° and running infrared spectra of the solution within 5 minutes.[19]

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(19)   A detectable amount of reaction occurred in this solution after 30 minutes at 0°.

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The infrared spectra show small remnants of the free hydroxyl band, the chlorocarbonate carbonyl, and the C-O-C stretching bands, a strong bonded hydroxyl and a carbonyl band with enhanced intensity at 5.48μ (Fig. 4 and 5). The amount of free alcohol and ethyl chlorocarbonate in the mixture was estimated from these spectra to be approximately 20% and increased on dilution; the amount of free pyridine could not be determined because of the weak absorption bands of this compound, but the bands were present. The results indicate more bonded alcohol and more complexed acid chloride in the three-component mixture in dichloro-methane than in the respective pyridine complexes of alcohol and acid chloride alone under the same conditions. This is explained tentatively by the formation of a three-component complex:

$$ROH \cdot Py \cdot R'COCl \rightleftharpoons ROH + Py + R'COCl$$
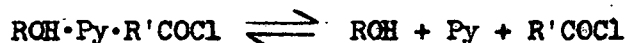
which would have a dissociation constant of the order of 0.0001.

Some conclusions concerning the nature of the three-component complex may be drawn from the infrared evidence. It is probably similar to the acid chloride·pyridine complex since absorption bands are observed at similar wavelengths. Both are very likely ionic and the experimental data can be accomodated if one assumes that in one case the acyl ion is stabilized by pyridine and in the other by pyridine·alcohol complex, i.e., that the band at 5.48μ is essentially a measure of solvated acyl ion.
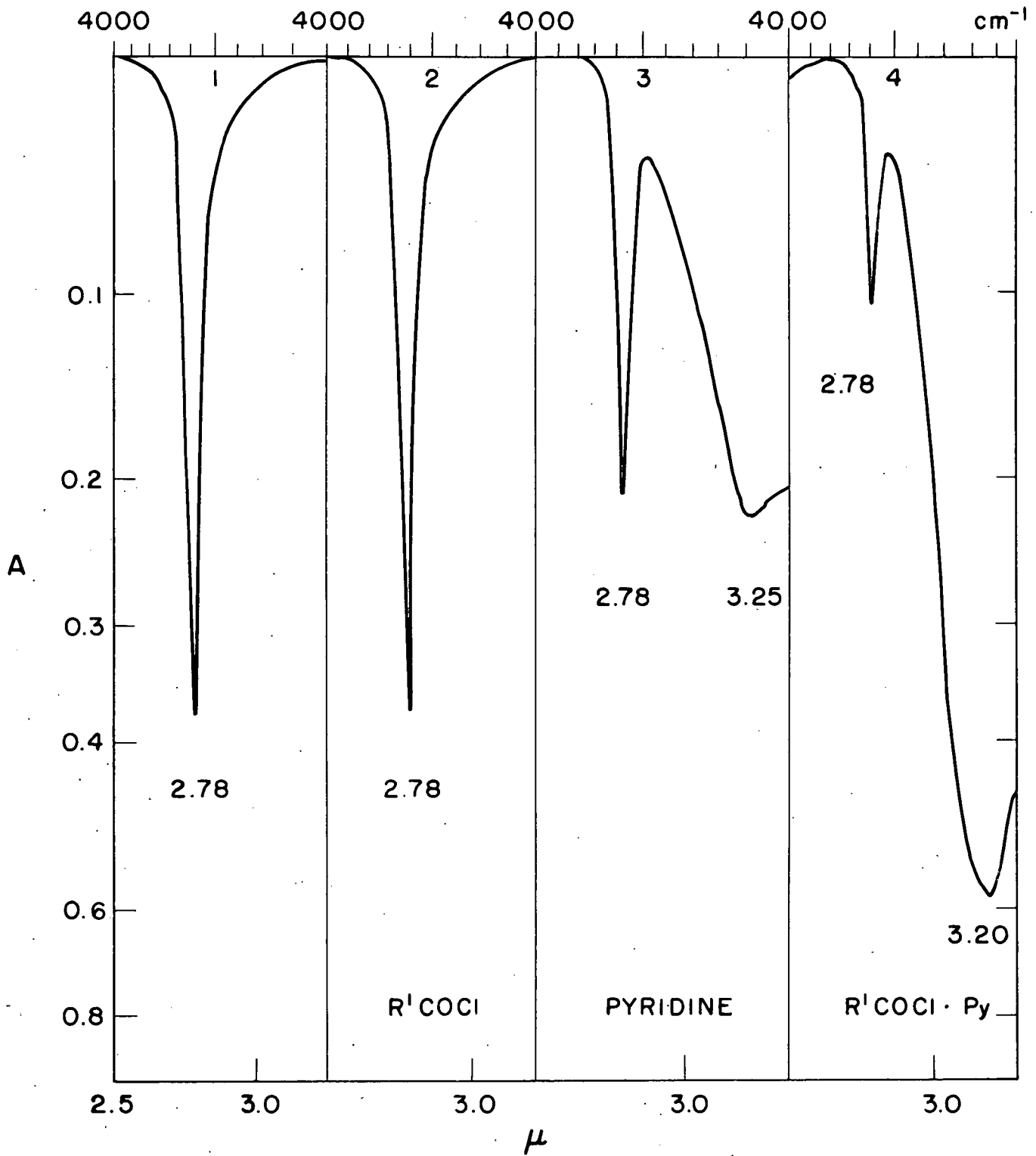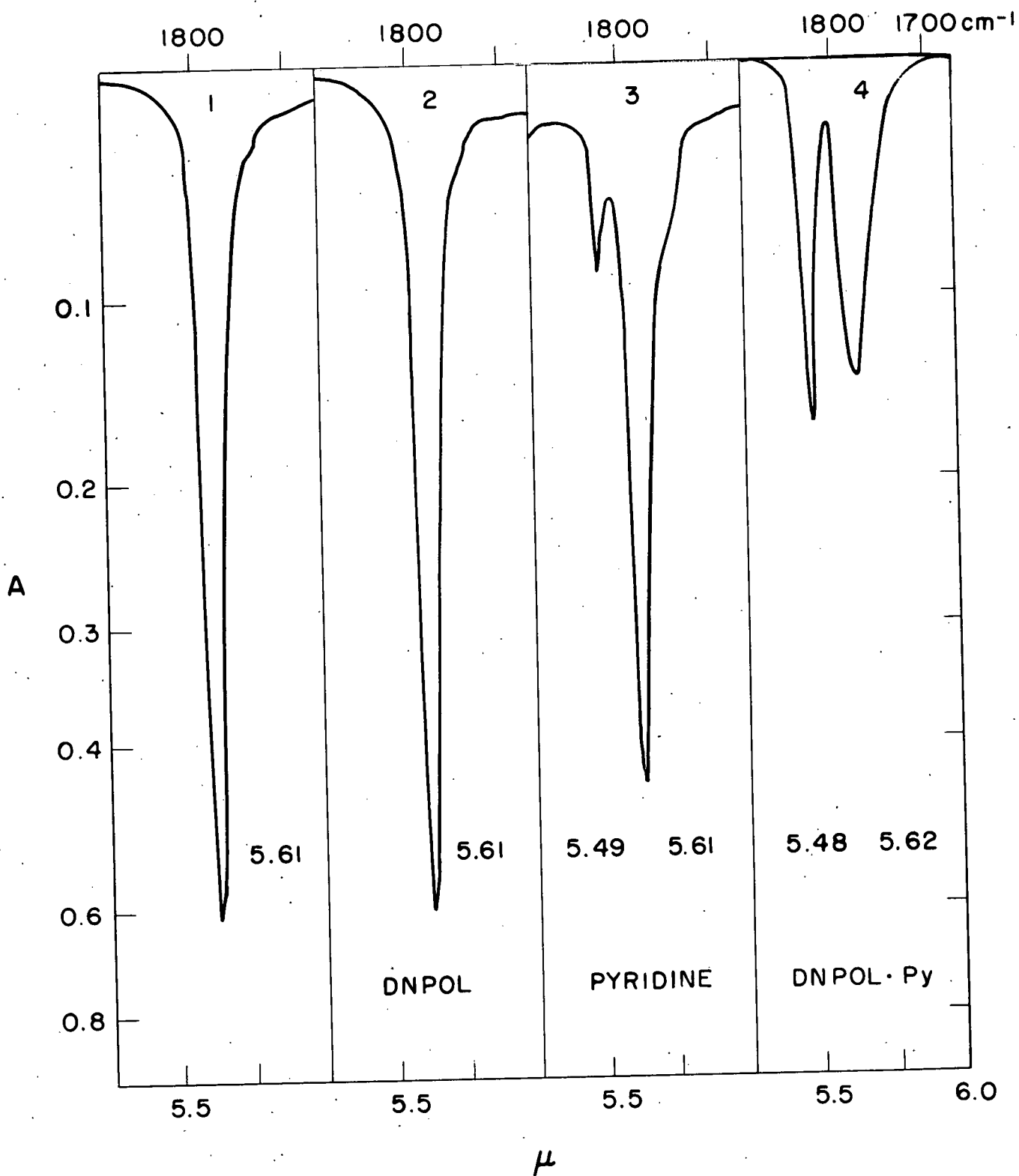
Fig. 4

Fig. 5

## Legends to the Figures

Fig. 1   Carbon tetrachloride solutions of 1:1 pyridine·alcohol, analytical concentration of the complexes versus concentration of free alcohols.

Fig. 2   Carbon tetrachloride solutions of 1:1 pyridine·alcohol, analytical concentrations of the complexes versus concentration of the undissociated complexes.

Fig. 3   Dichloromethane solution of dinitropropanol·10 pyridine, Y against $\dfrac{X}{A_{ROH \cdot Py}}$

Fig. 4   Infrared absorption bands for 0.1 M 2,2-dinitropropanol solutions in dichloromethane: 1. without addition  2. containing 0.1 M ethyl chlorocarbonate  3. containing 0.1 M pyridine 4. containing 0.1 M ethyl chlorocarbonate and 0.1 M pyridine, all in 0.05 cm cells against pure solvent.

Fig. 5   Infrared absorption bands for 0.1 M ethyl chlorocarbonate solutions in dichloromethane: 1. without addition  2. containing 0.1 M 2,2-dinitropropanol  3. containing 0.1 M pyridine  4. containing 0.1 M 2,2-dinitropropanol and 0.1 M pyridine, all in 0.01 cm cells.