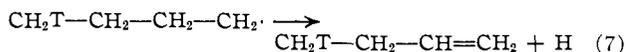
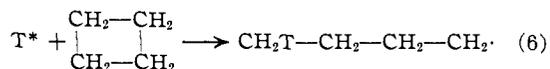


presumably from reactions 6 and 7



No conclusive statements are possible about the actual mechanism of reaction 7, which may involve an additional molecule, or may simply involve an energetic decomposition.

The butadiene, propylene and acetylene, however, come from especially energetic hot reactions and are not scavenger-sensitive.

Acknowledgments.—The cooperation of Allen Blotcky and the Omaha VA Hospital in performing the irradiations is gratefully acknowledged. Prof. W. D. Walters kindly furnished a small initial sample of cyclobutane for calibration purposes and exploratory experiments. Fellowship assistance was received by Edward K. C. Lee from the Pan American Petroleum Foundation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI 21, O.]

The Infrared Spectra and the Nature of the Bonding in Some (1-Pyridine N-Oxide)-3-Ethylene-2,4-dichloroplatinum(II) Complexes

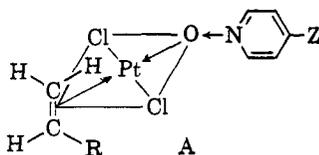
BY SAUL I. SHUPACK AND MILTON ORCHIN

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The N^+-O^- and $\text{C}=\text{C}$ stretching frequencies of a series of 1-(4-substituted-pyridine N-oxide)-3-ethylene-2,4-dichloroplatinum(II) complexes, structure A, were determined. The N^+-O^- band in the spectrum of each N-oxide is shifted to lower frequency on complexing with platinum; the extent of the shift increases with increasing electron-releasing properties of the 4-substituent. The $\text{C}=\text{C}$ stretching frequency also shifts to lower frequency, and in an essentially linear fashion, with increasing electron-releasing properties of the 4-substituent, thus demonstrating the transmission of electronic effects across the platinum atom.

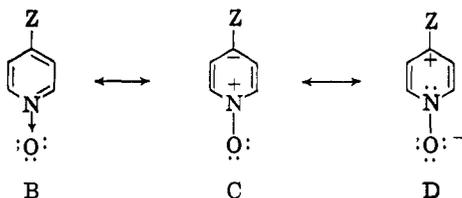
Introduction

Recent work in this Laboratory¹ showed that square planar complexes of platinum(II) of the general formula A can undergo exchange reactions in which the olefin or the N-oxide can be replaced by different olefins or N-oxides.



The infrared spectra of a series of these compounds (A, $\text{R} = \text{H}$; $\text{Z} = \text{NO}_2, \text{CO}_2\text{CH}_3, \text{Cl}, \text{H}, \text{CH}_3$ and OCH_3) has now been determined with a view toward securing information on the effect of ligand bonding as a function of the nature of Z.

Background.—Pyridine N-oxide can be represented by resonance forms C and D as well as by the principal structure B ($\text{Z} = \text{H}$)



The presence of electron-releasing groups (e.g., $\text{Z} = \text{OCH}_3$) would be expected to enhance contributions from structures such as D. Such groups should therefore lengthen the N^+-O^- bond and shift the infrared band associated with this bond to lower frequency as compared to the parent compound. Electron-withdrawing groups (e.g., $\text{Z} = \text{NO}_2$) should have the opposite

effect. The reported infrared spectra of the pyridine N-oxides in chloroform,² in Nujol mulls,³ and the spectra determined in the present work, Table I, confirm⁴ this expectation.

TABLE I

DATA FOR 4-SUBSTITUTED-PYRIDINE N-OXIDE AND STRUCTURE A ($\text{R} = \text{H}$)

Substituent	pK_a	σ_p	N^+-O^- , cm^{-1}			$\text{C}=\text{C}$, cm^{-1}
			Ligand	Complex	$\Delta\nu$, cm^{-1}	
OCH_3	2.05 ^a	-0.76 ^b	1210	1190	20	1490
CH_3	1.29 ^c	-0.31 ^b	1238	1224	14	1500
H	0.79 ^c	0	1242	1235	7	1510
Cl	0.36 ^d	0.23 ^b	1246	1238	8	1515
CO_2CH_3	-0.41 ^e	0.64 ^f	1252	1243	9	1528
NO_2	-1.7 ^c	1.27 ^c	1258	1250	8	1545

^a J. N. Gardner and A. R. Katritzky, *J. Chem. Soc.*, 4375 (1957). ^b Y. Okamoto and H. C. Brown, *J. Am. Chem. Soc.*, 79, 1913 (1957). ^c H. H. Jaffé and G. O. Doak, *ibid.*, 77, 4441 (1955). ^d Calculated using σ -value from footnote b and ρ -value from H. H. Jaffé, *J. Org. Chem.*, 23, 1790 (1958). ^e Calculated using σ -value from footnote f. ^f H. H. Jaffé, *Chem. Rev.*, 53, 191 (1953).

The effect of Z on the contributions from the various resonance structures also should be reflected in the basicity of the members of the series. Indeed, a linear relationship has been reported⁵ to exist between the pK_a of a series of 4-substituted-pyridine N-oxides and the Hammett σ -value of Z.

(2) J. N. Gardner and A. R. Katritzky, *J. Chem. Soc.*, 4375 (1958).

(3) G. Costa and P. Biasina, *Z. Phys. Chem. (Frankfurt)*, 4, 24 (1955).

(4) Our results, secured with mulls, corroborate the earlier work² except for the 4-nitropyridine N-oxide for which we obtained a doublet at 1258 and 1270 cm^{-1} as compared to the reported single band at 1271 cm^{-1} . A doublet in this region has also been reported² for chloroform solutions of 4-nitropyridine N-oxide except that the bands were at 1283 and 1294 cm^{-1} . For purposes of correlation of N^+-O^- stretching frequency we have chosen our 1258 cm^{-1} band because of its much greater intensity and because it appears from our correlations to be the band to be compared with other 4-substituted-pyridine N-oxides.

(5) H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.*, 77, 4441 (1955).

(1) L. García, S. I. Shupack and M. Orchin, *Inorg. Chem.*, 1, 893 (1962).

Results and Discussion

When pyridine N-oxide is complexed to platinum as illustrated in structure A, it would be expected that, because the oxide is a donor ligand, the N^+-O^- stretching frequency should be shifted to lower frequency irrespective of the nature of the Z group. The data in Table I and the plots in Fig. 1 show that with every substituent the N^+-O^- stretching frequency is shifted to lower frequency on complexing (solid curves) as compared to the same uncomplexed ligand (broken curves). Since the pK_a 's of the various pyridine N-

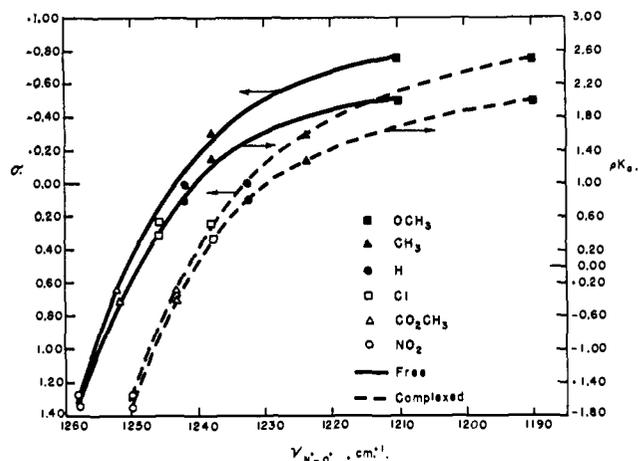


Fig. 1.— N^+-O^- frequency of free and complexed 4-Z-substituted pyridine N-oxides.

oxides vary linearly with the σ -value, it is to be expected that the same kind of curves are obtained when the N^+-O^- frequency is plotted against either pK_a or σ . The curves of Fig. 1 also show that the shift ($\Delta\nu$) is much greater for the electron-releasing groups OCH_3 and CH_3 than it is for the electron-withdrawing groups. This effect has its parallel in a variety of other properties of molecules. Thus, for example, the experimental dipole moments of nitrobenzenes are larger than the calculated vector sum of the individual group dipoles when electron-releasing groups (e.g., NH_2) are *para* to the electron-withdrawing nitro group.⁶ A similar incremental bathochromic effect in the 1L_a 203 $m\mu$ band of benzene is noted when groups which can reinforce electron shifts are substituted *para* to each other.⁷ The dipole and mesomeric moments of substituted pyridine N-oxides also show⁸ the incremental effects of strong electron-donating groups in the 4-position.

The similarity in the relationships of pK_a (and σ -values) to N^+-O^- frequency in both the free and complexed ligand indicates that the platinum in the complex plays the role of an electron acceptor in the same way as does a proton. The $Pt \leftarrow O$ bond is essentially a covalent σ -bond in which the p -electrons on oxygen are donated into the dsp^2 platinum orbital without any contribution from $d\pi-p\pi^*$ back donation. The orbitals on platinum of suitable symmetry, d_{xz} and d_{yz} , are filled and would be repelled by the lone pairs on oxygen. Interaction of the filled d -orbitals with antibonding orbitals around oxygen does not

(6) L. N. Ferguson, "Electron Structure of Organic Molecules," Prentice-Hall, Inc., New York, N. Y., 1952, p. 183.

(7) L. Doub and J. M. Vandenberg, *J. Am. Chem. Soc.*, **69**, 2714 (1947); **71**, 2414 (1949).

(8) A. R. Katritzky, E. W. Randall and L. E. Sutton, *J. Chem. Soc.*, 1769 (1957); C. M. Box, A. R. Katritzky and L. E. Sutton, *ibid.*, 1254 (1958).

occur, probably because the energy differences are too large. The absence of back donation is further indicated by the shape of the curve of the complexed ligand; this curve would tend to be more linear if back donation were a factor since such an effect would dampen the electron-releasing effect of Z.

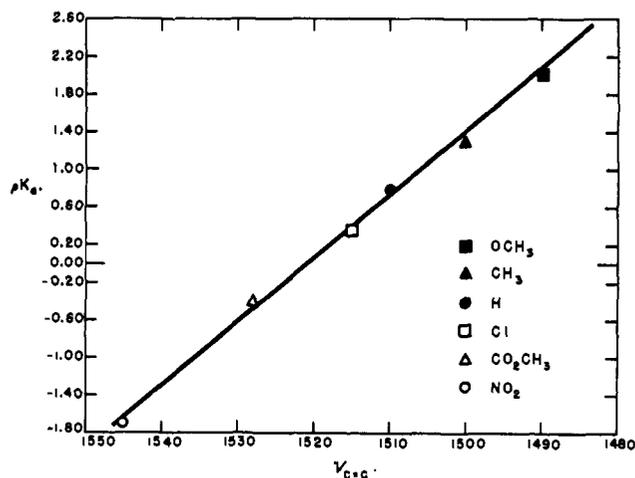


Fig. 2.— $\nu_{C=C}$ as a function of pK_a of 4-Z-substituted pyridine N-oxides.

Perhaps of even greater interest is the effect of Z on the $C=C$ stretching frequency of ethylene shown in Fig. 2. Free ethylene absorbs⁹ at 1623 cm^{-1} . Complexing with platinum usually shifts the olefinic stretching frequency about 140 cm^{-1} to lower frequency indicating a weakening of the $C=C$ bond. All pyridine N-oxides *trans* to ethylene also weaken the $C=C$ bond. Furthermore, those N-oxides with the strongest electron donors in the 4-position give the largest frequency shift. It is interesting that the relationship between the frequency shift and the pK_a of the corresponding free ligand is essentially linear. The effect of strong electron-releasing groups (e.g., $Z = OCH_3$) appears to be the strengthening of the platinum-olefin bond at the expense of weakening the $C-C$ bonding as a result of the enhanced population of the antibonding π^* -orbitals of the olefin. The kinetic implications of these conclusions are now being tested.

Experimental

All spectra were determined with a Baird KM-1 recording spectrophotometer using sodium chloride optics.

The pyridine N-oxides were prepared according to published procedures.¹⁰ The preparation of the complexes has been described earlier.¹¹ Properties of new complexes prepared for this work follow:

1-(4-Methylpyridine N-oxide)-3-ethylene-2,4-dichloro-platinum(II), A ($R = H, Z = CH_3$): light yellow crystals, m.p. (decomposition) 152°. Calcd. for $C_8H_{11}NO_2PtCl_2$: C, 23.8; H, 2.8; Pt, 48.2. Found¹²: C, 24.1; H, 3.0; Pt, 47.7.

Compound A ($R = H, Z = CH_3$): light yellow crystals, m.p. (decomposition) 155°. Calcd. for $C_8H_{11}NO_2PtCl_2$: C, 22.9; H, 2.6; Pt, 46.6. Found¹²: C, 23.0; H, 3.0; Pt, 46.7.

Compound A ($R = H, Z = CO_2CH_3$): gray-yellow crystals, m.p. (decomposition) 150°. Calcd. for $C_9H_{11}NO_3PtCl_2$: C, 24.2; H, 2.5; Pt, 43.6. Found¹³: C, 24.5; H, 2.5; Pt, 43.6.

Acknowledgment.—We wish to thank the Gulf Oil Corporation for a fellowship grant and Engelhard Industries for a generous supply of platinum.

(9) D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **13**, 69 (1958).

(10) E. Ochai, *J. Org. Chem.*, **18**, 534 (1953).

(11) L. Garcia and M. Orchin, *J. Chem. Soc.*, 2254 (1961).

(12) Gulf Research and Development Company.

(13) Galbraith Laboratories, Knoxville, Tenn.