# Investigation of Electronic Effects in the Pyridine and Pyridine *N*-Oxide Rings. Part 3.[1] Reactions of Substituted 2-Carboxypyridine *N*-Oxides with Diazodiphenylmethane †

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Rate constants for the reactions of diazodiphenylmethane (DDM) with a series of substituted 2-carboxypyridine *N*-oxides (3-, 4-, 5-, and 6-$CO_2Me$, 4-$NO_2$, 4-Cl, 4-Br, 6-Me, H, 4-OMe, 4-$NH_2$) have been determined in absolute ethanol over the range 20—50 °C. The existence of a strong intramolecular hydrogen bond has previously been established for this particular arrangement of the *N*-oxide and carboxy group, and it was previously believed that this type of interaction did not conform to the Hammett relationship. It was shown, however, that log(rate constants) for the reactions of 4-substituted derivatives are well correlated with ordinary $\sigma$ values of substituents with $\rho$ 1.340, and with a sliding scale of $\sigma$ values with $\rho$ 0.677. A satisfactory correlation was obtained between log(rate constants) for the reaction of a number of the above acids with DDM and the p$K_a$ values of the conjugate acids of correspondingly substituted pyridine *N*-oxides. On the basis of the results, it was concluded that an equilibrium between the hydrogen-bonded and the free acid precedes proton transfer in the rate-determining step in the reaction with DDM.

PREVIOUS investigations in this series [1] of the reactivity of carboxy-pyridines and -pyridine *N*-oxides with diazodiphenylmethane demonstrated the applicability of Hammett-type parameters to the reactions of the *N*-oxides. Satisfactory additivity of substituent effects was obtained, and it was possible to correlate, with the same regression line ($\rho$ 0.818, log $k_0$ 0.167, $r$ 0.993, $s$ 0.04, $n$ 17), the rate constants for both series investigated. The log(rate constant) values for the acids with substituents *meta* and *para* to the reaction centre, and *ortho* (for pyridine only), *meta*, and *para* to nitrogen and the *N*-oxyl group are correlated well with additive $\sigma$ values,[1b] $\sigma_N$ and $\sigma_{NO}$ being as previously reported.[1a]

Similar conclusions have been reached previously on the basis of the hydrolysis of substituted pyridinecarboxylates [2] and the solvolysis of pyridine analogues of t-cumyl chloride.[3] A more generalized interpretation of these last results and also a survey of other applications of the Hammett equation to the pyridine ring is given in an extensive review by Tomasik and Johnson.[4]

However, the values for substituted 2-carboxypyridine *N*-oxides were not correlated in the above manner, and this was attributed to the existence of an intramolecular hydrogen bond between the carboxy and the *N*-oxyl group. The existence of the intramolecular hydrogen bond in this case is not a matter for dispute, since this has already been established for vicinal *N*-oxyl and carboxy group is by i.r.[5] and $^1H$ n.m.r.[6] data. The i.r. spectra of 4-substituted quinaldinic acid *N*-oxides show very small and barely detectable absorptions in the 2 800—2 000 cm$^{-1}$ region, indicative of very strong intramolecular hydrogen bonding. Similarly, in a $^1H$ n.m.r. study of 2-carboxy-5-methylpyridine *N*-oxide and two 4-substituted quinaldinic acid *N*-oxides, the carboxy proton was found at very low field as a very broad and concentration-independent signal, a phenomenon typical of strong intramolecular hydrogen bonding.

## RESULTS AND DISCUSSION

Although the *N*-oxyl group can be formally treated as an *ortho*-substituent,[7] the existence of the intramolecular hydrogen bond and the unexpected negative value of $\sigma_{2NO}$ led to the limitations expressed as to its general applicability.[1a] To gain more evidence on this point we studied the reactions of a series of substituted 2-carboxypyridine *N*-oxides with diazodiphenylmethane in ethanol over the range 20—50 °C. A plot of the log(rate constant) values (Table, acids 2—10, $k_2$ at 30 °C) *versus* the additive $\sigma$ values showed a poor correlation ($\rho$ 1.89, log $k_0$ 0.288, $r$ 0.867, $s$ 0.30, $n$ 10) and considerable deviation from the $\rho$ value for other positional isomers.[1b]

Usually when intramolecular hydrogen bonding is significant the hydrogen is a constituent of a six-membered planar ring where all the other members have $\pi$-electrons associated with them.[8] In 2-carboxypyridine *N*-oxides this is essentially equivalent to the classical statement that such hydrogen-bonded rings can be drawn with two double bonds and with hydrogen acting in a divalent manner, although its position is unsymmetrical and further away from the bridged atom. This secondary bond is therefore the longest, and consequently, the weakest in the ring.[9] Therefore, it is reasonable to expect that any factor disturbing the electron density in the hydrogen-bonded ring would mostly affect the hydrogen bond itself, and the rate of the reaction with DDM, which involves proton transfer from molecular acids to DDM in the rate-determining step.[10,11] We considered that the most pronounced effect would be observed with substituents in position 4, entering into a direct interaction with the *N*-oxyl group [canonical forms (a) and (b) in the Scheme] as the more polarizable partner of the two groups forming the hydrogen-bonded ring. The electron density on the *N*-oxyl oxygen controls the equilibrium between the hydrogen-bonded and free form [(c) in the Scheme], the availability of hydrogen in the rate-determining breaking

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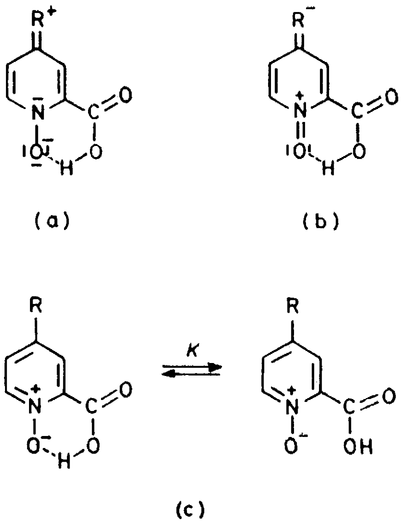
Rate constants for the reaction of DDM with substituted 2-carboxypyridine *N*-oxides

| Acid | Substituent | $k_2$/l mol$^{-1}$ min$^{-1}$ $^{a,d}$ 20 °C | 30 °C | 40 °C | 50 °C | $E^{\ddagger}$ $^{d}$/ kJ mol$^{-1}$ | log $A$ $^{c,d}$ | $\Delta S^{\ddagger}$ (30 °C) $^{d}$/ J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 3-$CO_2Me$ | | 39.60 | 50.18 | 95.60 | 37.33 | 6.254 | −133.64 |
| 2 | 4-$NO_2$ | | 4.61 | 11.71 | 51.85 | 100.23 | 16.161 | 56.62 |
| 3 | 5-$CO_2Me$ | 1.13 | 2.94 | 8.61 | 21.47 | 82.62 | 12.930 | −5.73 |
| 4 | 6-$CO_2Me$ | 1.20 | 2.68 | 5.13 | 10.80 | 57.92 | 8.633 | −88.11 |
| 5 | 4-Cl | | 2.16 | | | | | |
| 6 | 4-Br | | 1.68 | | | | | |
| 7 | 4-$CO_2Me$ | 0.37 | 1.47 | 3.48 | 8.74 | 73.90 | 11.127 | 40.36 |
| 8 | 6-Me | | 0.67 | | | | | |
| 9 | H | | 0.46 | | 1.58 | 49.78 $^{b}$ | 6.469 | −129.44 |
| 10 | 4-OMe | | 0.18 | 0.27 | 0.46 | 37.62 | 3.973 | −177.33 |
| 11 | 4-$NH_2$ | | 0.08 | | | | | |

[a] For the calculation of $E^{\ddagger}$ (from the slope of log $k_2$ *versus* $1/T$) and $\Delta S^{\ddagger}$, values of $k_2$ were expressed in l mol$^{-1}$ s$^{-1}$. [b] Rechecked value from Part 1.[1a] [c] Not calculated from the slope, but from the value of $k_2$ at 30 °C and $E^{\ddagger}$, as suggested by H. E. Avery, ' Basic Reaction Kinetics and Mechanism,' Macmillan, London, 1974, p. 53. [d] The rate coefficients are reproducible to ±3% (20—40 °C) and ±4% (50 °C) of the mean, normally from 3—6 runs. It is estimated that the maximum error which can arise from calculating $E^{\ddagger}$ in the stated temperature range is ±4 kJ mol$^{-1}$. The values of log $A$ and $\Delta S^{\ddagger}$ as calculated from $E^{\ddagger}$ vary very widely and it is estimated typically for acid 4 that their precision is ±0.63 log units and ±12.21 J K$^{-1}$ mol$^{-1}$.

of the O–H bond, and consequently the proton transfer from the carboxy group to DDM.

To test this hypothesis, and the eventual change in the reaction mechanism, we plotted the log(rate constant) values for the reaction of 4-substituted 2-carboxypyridine *N*-oxides against the $\sigma_p$ values for substituents in position 4. A very good fit to the log $k_2$–$\sigma_p$ plot was obtained (Figure 1) for a wide range of substituents. The elevated value of the reaction constant, ρ 1.34 (log $k_0$ 0.351, $r$ 0.999, $s$ 0.04, $n$ 7), by comparison with ρ 0.818 for other positional isomers using the same type of σ constants, indicates fairly large susceptibility to substituent effects of an equilibrium of the type (c) shown in the Scheme, in which breaking of the hydrogen bond precedes proton transfer from the acid molecule to DDM in the rate-determining step.



SCHEME Canonical forms for (a) electron donor and (b) electron acceptor substituents and (c) the equilibrium between the hydrogen-bonded and free form of 2-carboxypyridine *N*-oxides

For the substituents 4-$NO_2$, 4-OMe, 4-$NH_2$, and 4-$CO_2Me$ the values used were those calculated by McDaniel and Brown,[12] and 4-Cl and 4-Br were correlated by the use of $\theta_I$ values.[13] It appears that chlorine and bromine do not enter into a resonance type interaction with the *N*-oxyl group in the *para*-position, but this fits into the normal pattern of the behaviour of the heavier halogens.[13]

If equilibrium (c) takes place, log $k_2$ values should also be correlated with a sliding scale of σ constants in a manner similar to that used for p$K_a$ values of substituted 1-hydroxypyridinium ions [14] and also in numerous other investigations.[4] By using $\sigma^+$ for resonance donors and $\sigma^-$ for resonance acceptors, we obtained a very good correlation with ρ 0.677, log $k_0$ −0.247, $r$ 0.996, $s$ 0.07, and $n$ = 5. This plot is also given in Figure 1.

Furthermore, we considered that the set of data showing the above type of equilibrium dependence should be correlated with the p$K_a$ values for the conjugate acids of the corresponding substituted pyridine *N*-oxides.[14-16] Indeed, a fairly good straight line plot (Figure 2) is obtained with a regression constant of 0.338 ($r$ 0.985, $s$ 0.12, $n$ 6) which is very close to the ratio of reaction constants for the reaction with DDM and for the correlation with p$K_a$ values,[14] both obtained with ' sliding scale ' σ constants, $\rho_{DDM}/\rho_{pK_a} = 0.677/1.893 = 0.358$.

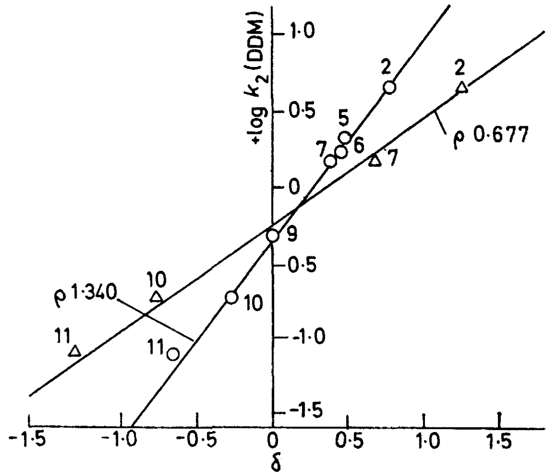


FIGURE 1 Relation between log $k_2$ for reaction of DDM with substituted 2-carboxypyridine *N*-oxides and δ constants of substituents (○, ordinary σ constants; △, ' sliding scale,' σ constants) (for key see Table)

This indicates that the ' sliding scale ' of $\sigma$ values is a more natural one, and essentially verifies the concept of equilibrium (c).

According to the well established mechanism (1) for the reaction of DDM with molecular acids, the rate-determining step involves slow proton transfer from acid to DDM and the formation of an ion-pair intermediate.[10,11,17] Therefore, if the steady state approximation is applied to the system, where AH and A–H

$$\mathrm{AH} + \mathrm{DDM} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A{-}H} + \mathrm{DDM} \xrightarrow{k_2} \mathrm{A^-{-}DDM{-}H^+} \xrightarrow{k_3} \text{Products} \qquad (1)$$

represent the acid in the hydrogen-bonded and free forms, respectively and $\mathrm{A^-{-}DDM{-}H^+}$ the ion-pair intermediate, we obtain equation (2) in a manner similar to that given by Johnson.[18] Therefore equation (3) obtains.

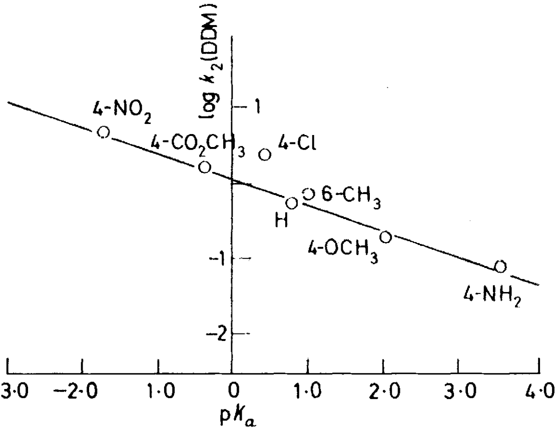


FIGURE 2 Relation between log $k_2$ for reactions of DDM with substituted 2-carboxypyridine $N$-oxides and the p$K_a$ of the conjugate acids of substituted pyridine $N$-oxides

Having in mind the existence of the above mechanism, it is very probable that $k_{-1} \gg k_2$, leading to equation (4). Taking the rate of reaction with DDM to

$$k_1[\mathrm{AH}][\mathrm{DDM}] = k_{-1}[\mathrm{A{-}H}][\mathrm{DDM}] + k_2[\mathrm{A{-}H}][\mathrm{DDM}] \qquad (2)$$

$$[\mathrm{A{-}H}] = k_1[\mathrm{AH}]/(k_{-1} + k_2) \qquad (3)$$

$$[\mathrm{A{-}H}] = k_1[\mathrm{AH}]/k_{-1} = K[\mathrm{AH}] \qquad (4)$$

be that of the formation of the ion pair, we finally obtain equation (5).

$$-\mathrm{d}[\mathrm{DDM}]/\mathrm{d}t = k_2[\mathrm{DDM}][\mathrm{A{-}H}] = k_2K[\mathrm{DDM}][\mathrm{AH}] \qquad (5)$$

The satisfactory plots in Figure 1 show that there exists a close internal correlation between the effects of substituents both on equilibrium (i) and on the rate of the reaction with DDM. No such relationship could be visualized from the calculated energies of activation and entropy changes given in the Table. It is to be expected that these parameters would vary very widely, both in magnitude and sign, in the equilibrium and reaction step, depending on the substituent.

To avoid possible ambiguity concerning the reaction centre of the esterification reaction, diphenylmethyl esters of 2-carboxy-4-nitro- and 2-carboxy-4-chloropyridine $N$-oxide were synthesized and identified (see Experimental section).

## EXPERIMENTAL

*Rate Measurements.*—Kinetics of the reaction of substituted 2-carboxypyridine $N$-oxides with DDM were studied as previously reported [1] by the spectroscopic method proposed by Roberts and his co-workers.[17] Optical density measurements were performed at 525 nm with 1 cm cells for absolute ethanol solutions at 30 °C. For the determination of $E^\ddagger$ and $\Delta S^\ddagger$, rate constants were also determined at 20, 40, and 50 °C. A Unicam SP 600 spectrophotometer was used.

Initially we attempted to study the reactions of substituted 2-carboxypyridine $N$-oxides with DDM as first-order processes, but this had to be abandoned because of the insolubility of the 4-NO$_2$ and 4-NH$_2$ derivatives. For those acids which were sufficiently soluble in ethanol (4-CO$_2$Me, 4-Cl, 4-OMe), a fairly good agreement between the second-order rate constants calculated from first-order values and those from direct measurement was obtained, if a ten-fold excess of acid was used.

Rate constants for all the compounds investigated (Table) were determined under second-order conditions and interpreted as before.[1,10] It should be noted that $\alpha$-values were abnormally low, which was also the case for 2,4-dinitronaphthol.[10] It is interesting that in this compound intramolecular hydrogen bonding between OH and NO$_2$ group forming a six-membered planar ring is also possible.

Because of the very low reactivity of the acids investigated, a long reaction time was necessary to obtain reliable data. The rate constants in the Table are mean values of up to six experiments. This is particularly true for values at 30 °C.

*Materials.*—Diazodiphenylmethane was prepared by Smith and Howard's method [19] and recrystallized from absolute methanol. Stock solutions (*ca.* 0.06M) were stored in a refrigerator and diluted for use.

*Solvent.* Good commercial grade absolute ethyl alcohol (Merck; water content 0.2%) was further treated with metallic sodium by the Smith method [20] giving a water content of 0.06% (g.l.c.).

2-Carboxy-4-nitropyridine $N$-oxide, m.p. 148 °C,[21] 2-carboxy-4-chloropyridine $N$-oxide, m.p. 144 °C,[21] 2-carboxy-4-methoxypyridine $N$-oxide, m.p. 154 °C,[21] and 2-carboxy-4-aminopyridine $N$-oxide, m.p. 217—218 °C,[22] were prepared by known methods and had m.p.s in agreement with those in the literature.

2-Carboxy-6-methylpyridine $N$-oxide, m.p. 180—181 °C (lit.,[23] 176 °C, by direct $N$-oxidation), was obtained by the KMnO$_4$ oxidation of 2,6-dimethylpyridine $N$-oxide (Fluka) by the method proposed by Kolarik.[24] 2,6-Dimethylpyridine $N$-oxide (22.1 g Fluka) and sodium carbonate (10 g) were dissolved in water (100 ml). A solution of KMnO$_4$ (60 g) in water (1 l) was added with mixing over 2 h. The solution was heated to 70 °C and stirred until the colour of KMnO$_4$ disappeared. Manganese dioxide was filtered off and the practically neutral solution was evaporated to 500 ml and left in a refrigerator overnight. A yellow-white precipitate crystallized out. Recrystallization from water and ethanol gave needles, m.p. 180 °C, test for $N$-oxyl group positive,[25] $\nu_{max.}$ (KBr) 1 230, 1 280 (NO), and 1 330 cm$^{-1}$ (Me) (Found: C, 53.95; H, 4.4; N, 9.2. Calc. for $C_7H_7NO_3$: C, 54.3; H, 4.6; N, 9.5%).

2-*Carboxy*-6-*methoxycarbonylpyridine* N-*oxide*. This was prepared by the method of Kolarik.[24] 2,6-Dicarboxypyridine *N*-oxide (Fluka; 2 g) was suspended in MeOH (60 ml) and cooled in an ice–salt mixture. A cold solution of diazomethane (*ca.* 4 g) in ether was added slowly with mixing and left overnight. Evaporation to dryness gave yellow-brown, oily crystals which were washed with ether and recrystallized from methanol to give *needles*, m.p. 123 °C, test for *N*-oxyl group positive,[25] $\nu_{max.}$ (KBr) 1 285, 1 245 (N–O), and 1 740 cm$^{-1}$ (C=O), weak absorption in the 2 800—2 000 cm$^{-1}$ region (hydrogen-bonded $CO_2H$ group) (Found: C, 48.6; H, 3.9; N, 7.25. $C_8H_7NO_5$ requires C, 48.7; H, 3.55; N, 7.15%).

2-*Carboxy*-5-*methoxycarbonylpyridine* N-*oxide*.[1a,26] This was prepared by the method of ref. 26, but the product had m.p. 162 °C (lit.,[26] 151 °C). Because of this discrepancy, another preparation was carried out. 2-Carboxy-5-methoxycarbonylpyridine (2 g),[27] glacial acetic acid (5 ml), and hydrogen peroxide (9 ml) were heated for 2 h in a thermostat at 50 °C. After cooling, water (10 ml) was added to the mixture, giving a precipitate. Recrystallization from methanol yielded fine crystals, m.p, 162 °C, which did not depress the m.p. of the product obtained according to ref. 26.

2-*Carboxy*-4-*bromopyridine* N-*oxide*. This was prepared by heating 2-carboxy-4-nitropyridine *N*-oxide [21] (2 g) and 47% HBr (40 ml) for 10 h at 110 °C. Evaporation to small volume under vacuum on a water-bath with several additions of water and ethanol to remove HBr, gave *material*, m.p. 149—150 °C (from ethanol) (Found: C, 33.0; H, 1.85; N, 6.55. $C_6H_4BrNO_3$ requires C, 33.05; H, 1.85; N, 6.4%).

2-Carboxy-4-methoxycarbonylpyridine *N*-oxide, m.p. 158—159 °C, was synthesized from 2,4-bismethoxycarbonylpyridine. Its preparation and identification will be reported elsewhere.[28]

*Diphenylmethyl ester of* 2-*carboxy*-4-*nitropyridine* N-*oxide*. The acid (0.5 g) was dissolved in absolute ethanol (20 ml) and an excess of DDM solution (0.06M) was added slowly with mixing. The colour of DDM disappeared with evolution of nitrogen. A fluffy precipitate formed after some time. Recrystallization from light petroleum (b.p. 50—70 °C; Fluka) gave crystals, m.p. 136 °C. Test for *N*-oxyl group positive.[25] The i.r. spectra was similar to those previously reported for diphenylmethyl esters of carboxypyridine *N*-oxides,[1a] $\nu_{max.}$ (KBr) 1 290, 1 276 (N–O), and 1 740 cm$^{-1}$ (C=O). The carboxy band (3 000—2 500 cm$^{-1}$) was absent (Found: C, 65.35; H, 4.1; N, 8.4. $C_{19}H_{14}N_2O_5$ requires C, 65.15; H, 4.0; N, 8.0%).

*Diphenylmethyl ester of* 2-*carboxy*-4-*chloropyridine* N-*oxide*. This was prepared as above, giving a light yellow precipitate, m.p. 151 °C [light petroleum (b.p. 50—70 °C)], $\nu_{max.}$ 1 270, 1 252 (N–O), and 1 740 cm$^{-1}$ (C=O). The carboxy band was absent, test for *N*-oxyl group positive [25] (Found: C, 67.25; H, 4.0. $C_{19}H_{14}ClNO_3$ requires C, 67.15; H, 4.25%).

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