The Infrared Spectra of Some Pyridones and Quinolones and Their Behaviour in the Kolbe–Schmitt Reaction.

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The cyclic amido-structure of 2-pyridone, 6-methyl-2-pyridone, 2-quinolone, and 4-methyl-2-quinolone in the solid state and in solution has been confirmed by infrared measurements.   The spectra of sodium 2-pyridyl oxide and potassium 2-quinolyl oxide have also been examined and a chelated structure for potassium 2-quinolyl oxide is suggested to explain its inertness in the Kolbe–Schmitt reaction.

IT is well known that the pyridones and analogous compounds are tautomeric with respect to the keto and the enol forms.   For 2-pyridone these are represented by (I) and (II) respectively, probably being stabilised by resonance with the dipolar forms (III) and (IV).

Following Auwers (*Ber.*, 1930, **63**, 2111) and Arndt (*ibid.*, p. 2963), Specker and Gawrosch (*ibid.*, 1942, **75**, 1338) showed by a study of the ultraviolet absorption spectra that in methanolic solution 2- and 4-pyridone exist substantially in the amido-form. Addition of alkali led to marked spectral changes which were ascribed to a change towards the enol form.   The spectrum of 3-hydroxypyridine, however, was not greatly affected by either alkali or acid.   Leis and Curran (*J. Amer. Chem. Soc.*, 1945, **67**, 79), on the basis of the dipole moment for a dioxan solution, concluded that in this solvent 4-pyridone

existed mainly in the pyridone form with an appreciable contribution from the dipolar form (V).

Although the infrared spectra of solid 3-hydroxy- and of 1-methyl-3-hydroxy-4-pyridone have been reported (Adams, Jones, and Johnson, *J. Amer. Chem. Soc.*, 1947, **69**, 1810) no information on the structure of the solid pyridones has been previously recorded. We have measured the infrared spectra of 2-pyridone, 6-methyl-2-pyridone and 3-hydroxypyridine

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\text{(I)} & \text{(II)} & \text{(III)} & \text{(IV)} & \text{(V)}
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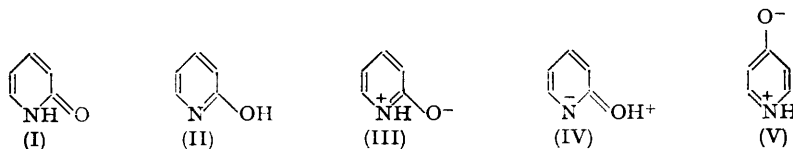
in Nujol and in potassium chloride discs (Hales and Kynaston, *Analyst*, 1954, **79**, 702), and the first two compounds as saturated and dilute solutions in chloroform and carbon tetrachloride. Both 2-pyridone (1571, 1600, 1645, and 1670 cm.$^{-1}$) and 6-methyl-2-pyridone (1543, 1612, 1657, and 1676 cm.$^{-1}$) as solids show bands in the 6-μ region which bear similarities to those exhibited by the pyrimidones and are indicative of the amido-structure. Thus Short and Thompson (*J.*, 1952, 168) have found that 1 : 4-dimethyl-2-methylthio-pyrimid-6-one has strong bands near 1596, 1651, and 1685 cm.$^{-1}$, whilst pyrimid-2-one has bands at 1620 and 1650 and pyrimid-4-one at 1605, 1660, and 1680 cm.$^{-1}$ (all as solids in Nujol). These investigators suggested that in the case of pyrimid-2-one one of these absorption bands arises from a carbonyl group of the lactam form, a second arising through an increase in value of the ring vibration localised in the C=N band owing to changes in the bond character resulting from the ketonisation. Absorption bands similar to those reported for the simple N-monosubstituted amides (Richards and Thompson, *J.*, 1947, 1248) are shown by 2-pyridone at 1571 and 1645 cm.$^{-1}$, these shifting in solution to 1540 and 1658 cm.$^{-1}$. 6-Methyl-2-pyridone behaves similarly. The possibility that intermolecular hydrogen bonding in the pyridones gives rise to the doublet around 1650 and 1670 cm.$^{-1}$ can be disregarded since dissolution in chloroform and carbon tetrachloride and dilution caused no shift or change in the intensity of those bands.

The evidence from the 3-μ region is inconclusive. Weak bands between 3100 and 3400 cm.$^{-1}$ are present in the spectra of the pyridones but cannot be regarded as definite proof of the presence of an amide group (cf. Short and Thompson, *loc. cit.*, p. 184). A stronger band near 3050 cm.$^{-1}$ probably arises from the aromatic C–H linkage since pyridine itself has an absorption band in this region. The spectrum of 3-hydroxypyridine shows the hydroxyl group to be present in bonded form since it has a very broad band centred at about 2430 cm.$^{-1}$. Presumably both OH $\cdots$ O and OH $\cdots$ N intermolecular bonding exist and this accounts for the wide spread of the absorption. The absence of strong absorption bands over the range 1600—1700 cm.$^{-1}$ confirms the absence of any possible keto-structure as with 2-pyridone. The insolublity of 3-hydroxypyridine in carbon tetrachloride and chloroform precluded measurement of the effects of dilution on the broad 2430 cm.$^{-1}$ band.

Ewing and Steck (*J. Amer. Chem. Soc.*, 1946, **68**, 2181), on the basis of ultraviolet absorption spectra, have also shown that 2- and 4-quinolones exist essentially in the amido-form in neutral or acid media. We have further confirmed those observations by studying the infrared spectra of 2-quinolone and 4-methyl-2-quinolone as solids and in solution. Both compounds show bands arising from an amido-structure and analogous to those observed for 2-pyridone. Thus 2-quinolone (solid) has bands at 1547, 1595, 1638, and 1654 cm.$^{-1}$, and in chloroform solution at 1553, 1605, and 1660 cm.$^{-1}$; 4-methyl-2-quinolone (solid) has bands at 1545, 1600, and 1644 cm.$^{-1}$, and in chloroform solution at 1548, 1605, and 1653 cm.$^{-1}$.

We have also examined the spectra of sodium 2-pyridyl oxide and of potassium 2-quinolyl oxide in the solid state. The structure of each of these compounds can be considered as the resonance hybrid of the various possible forms. Thus in the case of sodium 2-pyridyl oxide, if intermolecular chelation is assumed absent, contributions can be expected

from the completely covalent structures such as (VI) and (VII), and various ionic species such as (VIII), (IX), (X), and (XI). Neither of the two metal compounds mentioned shows absorption arising from a carbonyl group and this suggests that structure (VI) and its variants do not appreciably contribute toward stabilisation. Interaction of a positive sodium with nitrogen will however reduce the ionising tendency of the oxygen–sodium linkage and the overall behaviour of sodium 2-pyridyl oxide would appear best represented
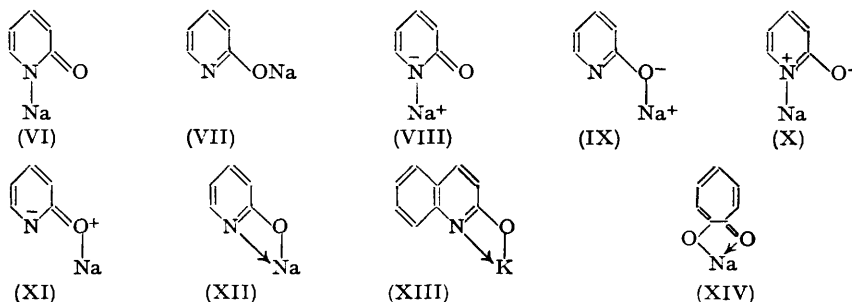
by structure (XII), in which weak chelation occurs between nitrogen and sodium. Rising temperature would presumably increase this interaction. Similarly potassium 2-quinolyl oxide can be represented by structure (XIII). Some support to these views is lent by the known chelation of alkali metals with salicylaldehyde (see, *e.g.*, Sidgwick and Brewer, *J.*, 1925, 2379), and some evidence to support a partially covalently bound metal atom is given by the observation that sodium 2-pyridyl oxide (m. p. 354—357°) and potassium 2-quinolyl oxide (m. p. 325°) both melt to clear orange-brown liquids, and both are soluble in hot anhydrous pyridine; they are however insoluble in boiling xylene.

The difficulty of carboxylating hydroxy-pyridines and -quinolines in the heterocyclic nucleus by the Kolbe–Schmitt reaction is reflected in the very few references in the elitrature. Tschitschibabin and Kirssanow (*Ber.*, 1924, **57**, 1161) reported that carboxyl-ation of sodium 2-quinolyl oxide did not occur under the normal Kolbe–Schmitt reaction conditions. However, because potassium 6-quinolyl oxide is more reactive towards carbon dioxide than the sodium compound (Schmitt and Altschul, *Ber.*, 1887, **20**, 2695) we have attempted to carboxylate potassium 2-quinolyl oxide under a variety of conditions but without success (see Experimental section). A chelated structure, such as (XII), particularly at elevated temperatures, and the consequent reduced mobility of the metal, would explain the much greater difficulty of carboxylating such metal compounds (cf. Hales, Jones, and Lindsey, *J.*, 1954, 3145); and in the case of sodium 2-pyridyl oxide the preferred carboxylation at the 5-position (Tschitschibabin and Kirssanow, *loc. cit.*; Baine, Adamson, J. W. Barton, Fitch, Swayampati, and Jeskey, *J. Org. Chem.*, 1954, **19**, 510). Similarly, for potassium 2-quinolyl oxide (XIII) the much reduced activity at position 3 and the blocking of position 5 prevent ready carboxylation. A similar inertness towards the Kolbe–Schmitt reaction has been reported for tropolone (Cook, Raphael, and Scott, *J.*, 1952, 4416) and here again it is probable that a chelated structure (XIV) prevents carboxylation. In the case of 3-hydroxypyridine intramolecular chelation cannot readily occur and good yields of both 2- and 6-carboxylic acids have been reported (Bojarska-Dahlig and Urbanski, *Roczniki Chem.*, 1952, **26**, 158; Jeskey *et al.*, *loc. cit.*).

EXPERIMENTAL

Microanalyses were carried out by Miss Corner and her staff of this Laboratory.

Infrared Absorption Spectra.—Spectra were measured on a modified Hilger D209 double-beam instrument (Hales, *J. Sci. Instr.*, 1949, **26**, 359; 1953, **30**, 52). Solid compounds were examined in potassium chloride discs (Hales and Kynaston, *loc. cit.*) and as mulls in Nujol. Mulls of hygroscopic materials were prepared in a dry box.

Ultraviolet Absorption Spectra.—These were measured for ethyl alcohol solution on a Unicam S.P. 500 Spectrophotometer.

Materials.—2-Pyridone, purified by repeated sublimation, had m. p. 106° (Found : C, 63·1;

H, 5·15; N, 13·9. Calc. for C_5H_5ON : C, 63·2; H, 5·3; N, 14·7%), $\lambda_{max.}$ 227·5, 299·0 mμ (log ε 3·90, 3·72).

3-Hydroxypyridine, purified by sublimation, had m. p. 125° (Found : C, 63·2; H, 5·4; N, 15·05. Calc. for C_5H_5ON : C, 63·2; H, 5·3; N, 14·7%), $\lambda_{max.}$ 218·0, 280·0 mμ (log ε 3·84, 3·68).

6-Methyl-2-pyridone, prepared by dehydrogenation of 6-methyl-2-piperidone over palladium black (Jones and Lindsey, *J.*, 1952, 3261) and purified by sublimation, had m. p. 159—160°.

2-Quinolone, purified by sublimation, had m. p. 200·5—201° (Found : C, 74·6; H, 5·1; N, 9·7. Calc. for C_9H_7ON : C, 74·5; H, 4·8; N, 9·8%), $\lambda_{max.}$ 230·0, 268·0 mμ (log ε 4·55, 3·82).

4-Methyl-2-quinolone, purified by sublimation, had m. p. 229—230° (Found : C, 75·6; H, 5·8; N, 8·8. Calc. for $C_{10}H_9ON$: C, 75·5; H, 5·9; N, 8·8%), $\lambda_{max.}$ 230·0, 268·0 mμ (log ε 4·57, 3·80).

Sodium 2-pyridyl oxide. 2-Pyridone (500 mg.) in methanol (5 ml.) was added to sodium hydroxide (210 mg.) dissolved in methanol (10 ml.). The methanol was removed under reduced pressure and the sodium 2-pyridyl oxide, as a white powder, was dried *in vacuo* at 130°; it had m. p. 345—347° (sealed tube) (Found : Na, 19·7. Calc. for C_5H_4ONNa : Na, 19·5%) and was readily soluble in anhydrous pyridine but insoluble in boiling anhydrous ether, toluene, or xylene.

Potassium 2-quinolyl oxide. This oxide, prepared as above and dried *in vacuo* at 160°, had m. p. 325° to an orange liquid (sealed tube) (Found : K, 21·9. Calc. for C_9H_6ONK : K, 21·3%). Potassium 2-quinolyl oxide was easily soluble in anhydrous pyridine but insoluble in boiling anhydrous xylene.

Attempted Carboxylation of Potassium 2-Quinolyl Oxide.—Potassium 2-quinolyl oxide was heated (i) at 214°/30 atm. (CO_2) for 3 hr., (ii) with anhydrous potassium carbonate, at 250°/36 atm. (CO_2), or in anhydrous pyridine at 200°/130—140 atm. (CO_2) for 6 hr. and 2-quinolone and anhydrous potassium carbonate were heated at 200—250°/60 atm. (CO_2) for 5 hr. No carboxylation occurred.

Infrared Spectra.—Absorption centres are given in cm.$^{-1}$; w = weak; m = medium; s = strong; sh = shoulder; bb = broad band. Nujol and solvent bands have been omitted.

2-Pyridone. (i) In KCl disc : 3060 m, *ca.* 2980 s, 1670 s, 1645 s, 1600 s, 1571 s, 1532 s, 1451 m, 1428 m, 1413 m, 1357 w, 1239 s, 1171 w, 1155 s, 1130 sh, 1097 s, 1008 m, 982 s, 962 sh, 926 m, 865 w, 845 w, 835 w, 781 s, 731 m. (ii) In Nujol : 3100 m, *ca.* 2925 s, 1680 sh, 1647 s, 1607 m, 1577 s, 1544 sh, 1435 s, 1368 sh, 1244 s, 1174 w, 1158 s, 1132 sh, 1098 s, 1008 m, 984 s, 962 sh, 926 m, 901 sh, 865 w, 846 w, 835 w, 782 s, 731 m. (iii) In carbon tetrachloride (dilute solution) : 3250 w, 3100 m, 2930 s, 2800 s, 1835 w, 1679 sh, 1658 s, 1618 s, 1473 m, 1437 m, 1372 w, 1248 s, 1152 m, 1096 m, 992 s, 924 m, 846 m. (iv) In chloroform (dilute solution) : 3350 w, 3250 w, 3100 m, 2800 s, 1672 sh, 1650 s, 1608 s, 1540 s, 1470 s, 1438 s, 1370 w, 1252 m, 1155 m, 1097 m, 1055 w, 993 s, 926 m, 849 m.

3-Hydroxypyridine. (i) In KCl disc : 2875 m, *ca.* 2430 s. bb, *ca.* 1780 s. bb, 1600 w, 1560 s, 1471 s, 1366 m, 1305 m, 1285 sh, 1274 s, 1236 s, 1209 sh, 1179 m, 1121 w, 1099 m, 1048 m, 1020 m, 926 w, 914 w, 905 w, 895 m, 848 m, 842 sh, 823 w, 806 s, 800 s, 703 s. (ii) In Nujol : *ca.* 2430 s, bb, *ca.* 1780 s, bb, 1600 w, 1563 s, 1458 s, 1368 s, 1309 m, 1287 sh, 1277 s, 1236 s, 1209 sh, 1178 m, 1121 w, 1098 m, 1046 m, 1019 m, 977 w, 914 w, 905 w, 894 m, 843 m, 828 m, 807 s, 800 s, 703 s. (iii) In chloroform (saturated solution) : 1580 w, 1279 m, 1099 w, 1050 w.

6-Methyl-2-pyridone. (i) In Nujol : 3100 m, 1676 s, 1657 sh, 1612 s, 1548 m, 1208 w, 1166 m, 998 m, 939 m, 927 m, 812 w, 800 m, 736 w. (ii) In chloroform (dilute solution) : 3350 sh, 3280 m, 3100 sh, 2800 s, 1965 w, 1858 w, 1776 w, 1650 s, 1622 sh, 1552 s, 1466 s, 1450 s, 1400 s, 1374 sh, 1160 m, 1034 m, 998 s.

2-Quinolone. (i) In KCl disc : 3060 m, 2970 m, 2825 m, 1654 sh, 1638 s, 1595 s, 1547 m, 1498 m, 1466 m, 1422 s, 1390 m, 1343 m, 1305 w, 1279 m, 1256 m, 1206 m, 1151 m, 1132 m, 1116 m, 1026 m, 981 w, 945 m, 923 w, 900 w, 864 m, 834 s, 774 m, 761 s, 831 m. (ii) In Nujol : 3100 sh, 1635 s, 1593 s, 1552 m, 1500 m, 1463 m, 1425 s, 1395 m, 1345 m, 1307 m, 1305 w, 1279 m, 1258 m, 1207 m, 1151 m, 1132 m, 1116 m, 1026 m, 981 w, 945 m, 924 w, 900 w, 864 m, 834 s, 774 m, 761 s, 831 m. (iii) In carbon tetrachloride (saturated solution ; very insoluble) : 1660 s. (iv) In chloroform (sat. solution) : 3350 w, 2820 s, 1660 s, 1605 s, 1553 m, 1422 s, 1342 w, 1279 m, 1261 m, 1152 m, 1138 m, 1120 m, 1028 m, 979 w, 943 m, 861 m, 831 s.

4-Methyl-2-quinolone. (i) In KCl disc : 3075 w, 2930 s, 2780 s, 1795 w, 1644 s, 1600 sh, 1545 m, 1500 m, 1425 s, 1383 m, 1364 m, 1342 w, 1258 w, 1203 w, 1157 w, 1140 w, 1070 w, 1031 w, 963 m, 929 m, 884 m, 864 m, 852 m, 767 w, 755 s, 746 s, 702 w, 663 m. (ii) In Nujol : 3100 sh, 2870 sh, 2720 sh, 1795 w, 1645 s, 1604 sh, 1554 m, 1506 m, 1430 s, 1390 m, 1369 m, 1350 w, 1261 w, 1205 w, 1160 w, 1143 w, 1071 w, 1034 w, 964 m, 931 m, 884 m, 864 m, 853 m, 765 w,

755 s, 745 s, 700 w, 663 m. (iii) In chloroform (saturated solution) : 3330 w, 2825 s, 1653 s, 1605 m, 1548 m, 1425 s, 1391 m, 1372 sh, 1342 w, 1261 m, 1070 w, 1033 w, 965 w, 945 w, 890 w, 870 m.

Sodium 2-pyridyl oxide. In Nujol : 1600 s, 1532 w, 1480 s, 1440 s, 1424 sh, 1353 s, 1283 m, 1228 w, 1194 w, 1143 m, 1095 w, 1035 w, 984 s, 955 w, 862 sh, 855 s, 832 w, 790 s, 737 s.

Potassium 2-quinolyl oxide. In Nujol : 3020 w, bb, 1605 s, 1542 s, 1498 s, 1424 s, 1302 m, 1288 m, 1256 m, 1243 sh, 1205 w, 1139 m, 1116 m, 1020 w, 964 w, 936 w, 922 w, 905 w, 864 w, 828 s, 796 w, 771 w, 758 s, 751 s, 731 m, 695 w.