Erratum: Heats of Combustion of Some Peroxides and the Heats of Formation of Acetate, Propionate, and Butyrate Radicals

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One of us, (J. O'M. B.) wishes to acknowledge the financial support of the Yardney Battery Company during the prosecution of this work.

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² P. G. Owston, Quart. Revs. **5**, 344 (1951).
³ Conway, Bockris, and Linton, J. Chem. Phys. **24**, 835 (1956).
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Comments and Errata

Erratum: Heats of Combustion of Some Peroxides and the Heats of Formation of Acetate, Propionate, and Butyrate Radicals

[J. Chem. Phys. **27**, 416 (1957)]

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THE first-named author was incorrectly listed as L. Jaffe. The correct name is I. Jaffe or Irving Jaffe.

Errata: B–Cl Distance in Boron Trichloride

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AS a test in a crystal structure of high symmetry of our general least squares program for orthorhombic, monoclinic, and triclinic space groups, we have further refined the hexagonal BCl_3 structure. The resulting shift of Cl by 0.06 A leaves the B–Cl bond distance at 1.75 A, and results in the revised parameters $x=0.052$ and $y=0.372$. Nonbonded $Cl\cdots Cl$ distances, revised to 3.87, 3.67, 3.83, and 3.90 A, are still normal. Values[1] of $R=0.111$ and $r=0.064$ were obtained for all observed reflections assuming hexagonal symmetry. The least squares treatment has rescaled the F_0 to 0.93 of their previously listed values. Reflections in decreasing order of their contributions to R in the previous study, with the new F_c in parentheses, are 311 (15.2), 420 (13.4), 130 (5.0), 211 (9.3), 132 (−4.6), 201 (−12.5), and 424 (9.2). For these reflections, the value of R has decreased from 0.51 to 0.17. The improvement is less, but significant, for the remaining reflections and no outstanding discrepancies now remain.

The space group is clearly $C\,6_3/m$, not $C\,6_3$, and the molecule lies in the mirror plane. Atomic z coordinates are at $z=0.25$, not $z=0$, and the signs of reflections for $l=2$, 3, 6, and 7 must be reversed. The discrepancies of structure factors previously ascribed to anisotropic thermal motion are to be ascribed to incomplete refinement in the earlier study.

¹ Dickerson, Wheatley, Howell, and Lipscomb, J. Chem. Phys. **27**, 200 (1957).

Notes

Ultraviolet and Infrared Absorption Spectra of 4-Methoxypyridinium Salt

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4-METHOXYPYRIDINE is known to be expressed by the resonance between the usual structure and the polar one in which one of the lone-pair electron of the oxygen atom outside the ring transfers to the π orbital of the nitrogen atom (Fig. 1).* When the nitro-

FIG. 1.
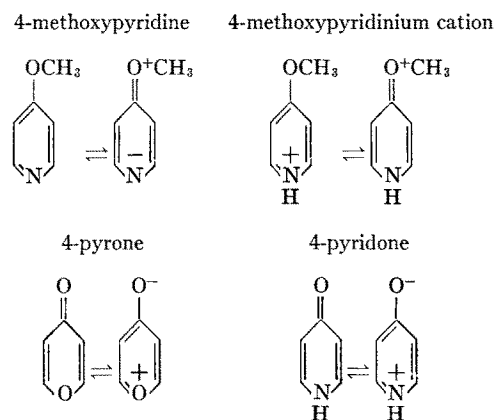
gen atom of 4-methoxypyridine is coordinated with proton, namely when 4-methoxypyridinium salt is formed, the contribution of the latter may conceivably increase because of the increased electronegativity of the nitrogen atom, and its π-electronic structure may be expected to approach to those of pyridone or pyrone. On the basis of this expectation, we have investigated the ultraviolet and infrared absorption spectra of 2,6-dimethyl-4-methoxypyridine (DMP) and related compounds, by use of a Beckman Model DU and a Perkin Elmer Model 112 spectrophotometer, respectively.

The near ultraviolet spectrum of DMP in methanol or aqueous solution has a characteristic feature of the 4-

substituted pyridines: a weak band with several sub-maxima appears at the same wavelength region as that observed with pyridine itself.[1] But its spectrum changes markedly in the acidic medium (0.1 N HCl), showing an intense band at 236 mμ. The same result was obtained in the solvent with the higher concentration of HCl (1 N HCl). This means that this band can be due to the DMP cation in which a proton is attached to the nitrogen atom of the pyridine ring. It seems interesting that this band is similar in its wavelength and intensity to that observed with pyridone and pyrone as is easily seen from Table I. The most plausible interpretation of

TABLE I. Near ultraviolet absorption spectra.

	λ_{max} mμ	ϵ_{max} cm^{-1} mole^{-1} l
2,6-dimethyl-4-pyrone	245	17 000
4-pyridone[a]	255	16 000
2,6-dimethyl-4-methoxy-pyridinium cation	236	10 000

[a] H. Specker and H. Gawrosch, Ber. deut. chem. Ges. 75B, 1338 (1942).

these bands is that they are the intramolecular charge transfer absorption band[2] accompanied by the electron transfer between the π orbital of the oxygen atom outside the ring and that of the ring.†

The results of the infrared measurements are shown in Table II, where all measurements are made with the

TABLE II. Observed frequencies of the infrared bands related with C=O and ring stretching vibrations in cm^{-1}. s, m, and w denote strong, mild, and weak, respectively.

2,6-dimethyl-4-methoxypyridine		1598 s	1577 s	1462 s
2,6-dimethyl-4-methoxy-pyridinium picrate[a]	1656 m	1616 s		1495 m
pyridinium picrate[a]		1597 s	1563 s	1485 m
2,6-dimethyl-4-methoxy-pyronium chloride	1654 s	1575 w	1555 s	1487 s
2,6-dimethyl-4-methoxy-pyronium methperchlorate	1654 s		1552 s	1494 s
2,6-dimethyl-4-pyrone	1669 s	1612 s	1584 s	1457 m
4-pyridone[b]	1630 s		1542 w	1515 s

[a] Here, the bands whose frequencies coincide with those of the bands of crystalline picric acid are excluded.
[b] Y. N. Sheinker and Y. Z. Pomerantsev, Zhur. Fiz. Khim. 30, 79 (1956).

Nujol mull of the crystalline samples. It is known that the stretching vibration bands of substituted benzenes and six- or five-membered heterocyclic compounds usually arise in the region between 1600 cm^{-1} and 1450 cm^{-1}. As shown in the table, pyrones and pyridones, as well as pyronium salts, show infrared bands near 1650 cm^{-1} and these bands are interpreted as due to the conjugated C=O bonds. It has been found that the picrate of DMP also have a band at 1656 cm^{-1}. As picric acid itself shows no band in this region, it can be concluded that this band is due to the DMP cation. Moreover, pyridinium picrate has no band in such a wavelength region.

Then, it may be concluded that the C−O bond in DMP cation is responsible for the 1656 cm^{-1} band, and, therefore, that the bond has a large double bond character. This conclusion is apparently consistent with the above-mentioned fact that the ultraviolet absorption of DMP cation is similar to those of pyrone and pyridone.

The author wishes to express sincere thanks to Professor S. Nagakura for his kind encouragement and valuable advice during the course of the present work.

* Rigorously speaking, there are several other resonance structures of considerable importance. But this does not matter for the discussion in the present paper.
† Besides the charge transfer state, however, the excited state of the ring π electrons similar to the B_{1u} state of benzene seems to participate, to some extent, in the upper state.
[1] Relations between the position of substitution and the ultraviolet absorption spectra of substituted pyridines are discussed in the earlier paper: H. Tsubomura, J. Chem. Soc. Japan, Pure Chem. Sec. 78, 293 (1957).
[2] A concept developed by S. Nagakura et al. for interpreting some of the strong absorption bands of aromatic or conjugated chain compounds. See, for instance, S. Nagakura, J. Chem. Phys. 23, 1441 (1955); J. Tanaka and S. Nagakura, J. Chem. Phys. 24, 1274 (1956).

Proton Magnetic Resonance Studies of the Acetic Acid, Phenol, and Water in Mixtures with Pyridine

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RESEARCHES on the physico-chemical properties of binary system of pyridine and acetic acid have been done by various workers. Recently Venkatesan and Suryanarayana[1] showed that the equivalent conductivity, viscosity, contraction in volume, and refractive index in this system exhibit a maximum at the composition of 83 mole percent of acetic acid, and pH also has an inflection point at the same composition. Barrow[2] showed that the 1:1 reaction product between pyridine and acetic acid in chloroform is a simple hydrogen-bonded complex.

We have carried out proton magnetic resonance experiments with the binary systems of acetic acid-, phenol-, and water-pyridine, respectively. The NMR spectra were obtained with a Varian V-4300B High Resolution Spectrometer at a fixed frequency of 40 mc/sec. The sample was sealed in a 5-mm o.d. tube. The scale of the chemical shifts in cps were calibrated by 227 cps, the separation between the proton signals of benzene and cyclohexane in equal volume mixture.

The results were shown in Figs. 1, 2, and 3. In every case, the mixture at a composition of about 50 mole