PROTONATED γ-PYRONES*†

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ABSTRACT

The vibrational spectra of several salts of 4-pyrone and 2,6-dimethyl-4-pyrone have been measured in the solid state. Deuterium replacement has been used to identify motions of the hydrogen atom which is located on the carbonyl oxygen atom and forms a hydrogen bond with the anion.

Bands due to OH stretching vibrations have been observed from 2086 cm^{-1} in the HCl salt to 3310 cm^{-1} in the hexachloroantimonate of 2,6-dimethyl-4-pyrone. In-plane hydrogen-deformation modes of the OH group have been found near 1300 cm^{-1} with a much smaller range in the different salts than the stretching vibration. For the 4-pyrone salts the OH stretching vibrations were at similar frequencies, and the in-plane hydrogen-deformation frequencies were close to 1340 cm^{-1}. Bands due to the out-of-plane deformation were not observed.

Aqueous solutions of 2,6-dimethyl-4-pyrone hydrochloride at various concentrations showed the presence of both protonated and neutral molecules.

INTRODUCTION

A comparison of the vibrational spectra of several Lewis acid complexes of 2,6-dimethyl-4-pyrone with that of the pyrone hydrobromide has clarified the assignments of γ-pyrones and also shown that the carbonyl oxygen atom was the basic site and not the heterocyclic oxygen atom (1).

These results are part of a general emerging pattern which shows, contrary to previous views, that carbonyl oxygen atoms can often be more basic than ether oxygen atoms. The circumstances leading to enhanced basicity in carbonyl groups have been discussed in detail (2, 3). The γ-pyrones satisfy most of the required conditions.

The basic nature of the γ-pyrones has been known for over 50 years since the pioneering work of Collie and co-workers (4). The structural details, however, were clouded by new conceptions on the quadrivalence of oxygen, based on ultraviolet absorption spectra (5), then a newly emerging art. Thus the heterocyclic oxygen atom was regarded as the basic site, partly by analogy with the alleged salt of dimethyl ether with HCl, which showed up as a dystectic point in an equimolar mixture of the two components (6). The concept of the hydrogen bond was not, of course, known at that time.

With the advance of modern spectroscopic methods, coupled with a fund of knowledge of spectroscopic behavior of many compounds, came a re-evaluation of the situation. Wolkenstein and Syrkin (7) examined the Raman spectrum of 2,6-dimethyl-4-pyrone hydrochloride in aqueous solution, and after noting little difference between the salt and the pyrone pronounced the carbonyl group as the protonation site. Similar conclusions were reached by Kahovec and Kohlrausch (8). The infrared spectra of several thiapyrones were recorded by Tarbell and Hoffman (9), who favored protonation of the carbonyl group in salts of such compounds. Phillips (10) deduced from the Raman spectrum of an aqueous solution of 4-pyrone hydrochloride that protonation was most likely to occur at the carbonyl oxygen atom. Tsubomura (11) also commented on some

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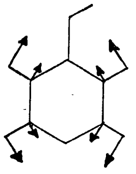
similar compounds. Crystallographic data for the hydrobromide (12) revealed a monoclinic crystal with the following parameters: $a = 6.89$ Å; $b = 15.52$ Å; $c = 15.51$ Å; $\beta = 94.9°$. There were eight molecules per unit cell.

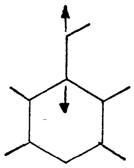
In order to make confident assignments for the vibrations involving the proton a series of γ-pyrones salts has been prepared, along with some deuterated analogues, and their infrared spectra recorded with a prism-grating spectrometer.

RESULTS AND DISCUSSION

2,6-Dimethyl-4-pyrone Salts

The infrared absorption bands in the various recorded spectra are collected in Table I. As shown previously (1) the bands near 1490 cm^{-1} are due to carbonyl stretching vibrations (II), the 1645 cm^{-1} bands being the C=C stretching mode, or a ring vibration having these characteristics, as in I. The strong band near 1555 cm^{-1} must also be due to a ring mode (III) involving stretching of C=C bonds (see below).


(I)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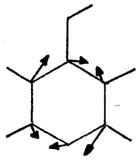
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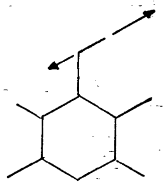
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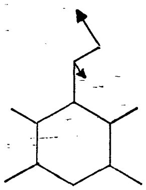
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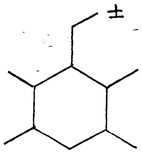

(VI)

The prominent feature in the spectrum of the hydrochloride at 2086 cm^{-1}, with several subbands on either side, can only be due to the motion of a hydrogen atom attached to the carbonyl oxygen atom (IV). Its breadth, intensity, and position are all consistent with a strong interaction between the hydrogen atom and the halide ion. The frequencies and approximate half-widths of these bands for different anions are collected in Table II.

The behavior on deuteration has been observed for many of the salts studied and is quite characteristic of hydrogen bond formation. The OH bands move to lower frequencies, as shown in Table II, with a ratio of $\nu_{\mathrm{OH}}/\nu_{\mathrm{OD}}$ close to 1.3. This is in keeping with a fairly pure hydrogen stretching motion.

The behavior of a protonated molecule forming a hydrogen bond with an anion had been discussed previously for pyridinium salts (13 and references therein to other systems). The pyrone salts presently considered exhibit a very similar behavior to the pyridinium series. As the size of the anion increases and the force field weakens the band attributed to the OH stretching vibration recedes to higher frequency. However, there is not a great deal of evidence of significant sharpening of the bands, as some half-widths in Table II show. Nor is there any gross change in the intensity of the band in its passage to higher frequencies. While these measurements of intensity and half-width can be at best only a rough guide, they should be internally consistent. The half-widths in the deuterated compounds, however, do show a significant decrease.

The in-plane hydrogen-deformation mode (V) has been assigned to a medium-strong band which occurs near 1300 cm^{-1} in most of the compounds. On deuteration this moves to about 1000 cm^{-1}, the ratio δ_{OH}/δ_{OD} being, again, about 1.3, showing that the vibration is a reasonably pure one with little coupling with other modes (see Table III). The other vibration with which the in-plane hydrogen-deformation mode might be expected to couple is the carbonyl vibration which is at about 1490 cm^{-1}. In alcohols, and probably phenols, coupling between ν_{CO} and δ_{OH} is likely, since both have similar force constants and frequencies. In the present case, however, a separation of about 190 cm^{-1} is sufficient to preclude serious interaction, as is shown by the negligible change in ν_{CO} on deuteration.

It has been asserted that strong hydrogen bonds are associated with low stretching frequency and high bending frequency of the XH bond. In the series of pyridinium salts recently described (13) only a very rough relation was found between ν_{NH} and δ_{NH}. In the present case similar behavior was observed. A plot of ν_{OH} against δ_{OH} revealed a general trend with an inverse proportionality but with a wide scattering of points.

Accompanying the 1300 cm^{-1} band a weaker absorption near 1240 cm^{-1} was always present. This band moved to lower frequency on deuteration, to near 945 cm^{-1}, the ratio being about 1.3, showing a fairly pure vibration. The possibility that this could be an overtone of a strong band near 600 cm^{-1}, perhaps due to a torsional OH (or out-of-plane) motion, was discounted since no strong band in this region was found when a spectrum was recorded on an instrument without the limitations of NaCl optics. The assignment to a CD bending mode was also rejected since no stretching vibration was visible, and there is evidence that the hydrogens in the 3-position in 2,6-dimethyl-4-pyrone do not readily exchange (10). Coupling of the deformation mode in the unit cell seems the most likely cause of the splitting of this band, especially since the unit cell of the HBr salt is known to contain eight molecules (12).

The in-plane hydrogen-deformation mode being reasonably well assigned, an out-of-plane bending mode would be expected. No band has been found, however, in the appropriate place and with the right shift on deuteration. It must be concluded that this band is too low in frequency to be observed on a spectrometer equipped with sodium chloride optics.

Several other assignments are suggested in Table I, based on previous experience (1) and by comparison with similar molecules (10).

Aqueous Solutions of 2,6-Dimethyl-4-pyrone Hydrochloride

Previous studies of the Raman spectra of aqueous solutions of γ-pyrone salts (7, 8, 10) revealed very small differences between the spectra of the neutral pyrone and the salts. These small differences resulted in the assignment of the carbonyl oxygen atom as the probable protonation site. In view of the obvious differences between the infrared spectra of the neutral molecule and the salts, the aqueous solution spectra were required to explain these conflicting views. The bands in the spectra of aqueous solutions are shown in Table IV.

The spectrum of 2,6-dimethyl-4-pyrone in aqueous solution shows clearly two main strong bands at 1660 and 1582 cm^{-1}. These are assigned respectively to the ring mode I and the carbonyl vibration. The lower value of ν_{CO} in aqueous solution must be due

TABLE

	4-Pyrone									
	Cl⁻		Br⁻		Cl⁻		Br⁻		I⁻	
	H	D	H	D	H	D	H	D	H	D
	3125w		3130w							
ν_{CH}	3070m		3067m		3070w	3075w			3052m	3050w
ν_{CH}	3050m, sh		3055w, sh		3044w	3050w	3040w	3040w	3040w	3020w
ν_{CH_3}					2993w	2998w	2990w	2990w	2988w	2987w
ν_{CH_3}					2913w	2913w	2910w	2910w		
			2658w				2655w	2025w		
			2608w							
			2572w	2070m			2550m	1970m	2850m	
			2518m	2002m			2438m	1911m	2745s, sh	2175w
			2435m	1939w	2149m, b		2404s	1870s, b	2720s, sh	2121m
ν_{OH}	2128s, b		2380m	1880s	2086m, b		2380s, b	1860s, b	2695vs, b	2079s
	2108s, b		2250w	1780w					2558s	1980m
	2040m			1756w	2050m, b				2491s	1920m
	1954m				1975m				2467s	1872m
	1838m, sh				1860m				2411m	
	1813m									
	1780m, sh									
	1765s				1788s					
			1630s, sh	1630s, sh	1655w, sh	1655m, sh	1658m, sh	1658m, sh	1655m, sh	1655m, sh
	1627s	1625s	1623s, sh	1623s, sh	1623s, sh	1637vs	1639vs	1639vs	1649s, sh	1650s, sh
ν_{CC}	1610s	1612s	1619s	1619s	1630vs	1633vs	1633vs	1630vs	1640vs	1639s
										1630s, sh
	1596s, sh	1595m, sh				1562w	1562w	1562w	1560m, sh	
ν_{CC}	1547m		1548m	1548m	1550s	1548s	1548s	1546s	1547s	1548s
		1528w		1530m	1540m, sh		1542s	1542s	1540s, sh	1542s
	1510m, sh	1510s, sh	1508m, sh							
	1500s, sh	1499vs								1490s, sh
ν_{CO}	1492vs	1495s, sh	1494s	1494s	1490s	1484s	1484s	1488s	1480s	1480s
	1485s, sh	1488s, sh	1490s, sh	1490s, sh					1470s, sh	1473s, sh
δ_{CH_3}					1416m	1412m	1417w	1420w	1411w	1409m
	1350s	1357m	1344m	1344m	1382m	1386w	1383w	1382w	1382w	1380w
					1360w	1362w	1359w	1355w	1359w	1357w
δ_{CH_3}					1326s	1320s	1329m	1329m	1329m	1328s
								1307w		
δ_{OH}	1343s, sh	1003s	1339m	988m	1316s	1010m	1307w	1002m	1290m	996m
		1320m		1318m						
δ_{CH}	1298s	1301m	1290s	1288s						
		1229m		1226m		1232m		1235w	1255w	
δ_{OH}	1209m	1058m	1203m	1052w	1210w		1209m	948m	1203m	939m
									1188w	1185w
δ_{CH}	1185s	1188s	1185s	1183s	1179s	1180s	1176s	1175s	1172s	1172s
					1072w		1074w	1070w		
					1046w	1048m	1046w	1046w	1044w	
ν_{CC}	1030w	1032m	1029w	1030m	1031m	1034m	1031m	1030m	1030m	
					973m	972m	976m	972m	978m	974m
δ_{CC}	941s	943vs	944s	943s	956m	956m	966w	948m	966w	
					921m	924m	921m	920m	920m	918m
			870m	883m	903m	904m	903m	896m	889m	888m
	861s	864s	858s	860s	895m	898m				885m, sh
δ_{CC}	848s	840m	847s	846s	866m	872m	854m			
			834m	840m						
				731w						
	658w	658w		660w		685m				

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		2,6-Dimethyl-4-pyrone									
$HgCl_3^-$		ClO_4^-		$TiCl_6^=$	$ZrCl_6^=$	$SnBr_6^=$		$SnCl_6^=$	$PtCl_6^=$		$SbCl_6^-$
H	D	H	D	H	H	H	D	H	H	D	H
		3084m	3082m	3072m	3080s	3074s	3069m	3078s	3065m	3069m	3077w
3055w	3056w								3057m	3058m	
2895m, b	2200w, b										
2810m, b	2153m, b	2962m, b	2230m, b	3050s, b	3100s, b	3100s, b	2320mb	3100s, vb	3152s, vb	2350s, b	3310s, b
2740m, b	2120m	2940m, b		2602w							
2608m	1995w	2840w, b		2510w							
2515m	1938w										
									1655s, sh	1656s, sh	
1654s, sh	1655s, sh		1655vs	1653vs	1656vs	1658s, sh	1655m, sh	1654vs	1650vs	1650vs	1653vs
1646vs	1648vs	1655vs	1648vs	1650vs	1650vs	1651vs	1648vs	1650vs	1644vs	1644vs	1648vs
1640s, sh						1645vs	1642vs	1638m, sh	1638m, sh	1638s, sh	
1560m, sh	1560m, sh	1560s, sh	1560m, sh	1560s	1563s	1565s	1560m, sh	1562s	1561s	1561s, sh	1560s
1548m, sh	1548m	1550s, sh	1547s	1558s	1548s	1548s, sh	1551s	1559s		1552s	1555s
1538m	1540m, sh	1540s	1539s	1542m			1540s, sh	1542m	1542s	1547s	1540s
					1510w	1490s, sh	1490s, sh		1490m, sh	1490m, sh	1491s
1483s	1487s	1481s	1487s	1488m	1490s	1486s	1480s	1489s	1482s	1481s	1488s
1475s, sh					1477m, sh	1475m, sh	1475m, sh	1475m, sh	1475s, sh	1472s, sh	
1410w	1408w	1416m	1410m	1406w	1412m	1412w	1408w	1412w	1412w	1410w	1406w
1380vw	1380w	1360w	1360w		1380w	1380w	1378w	1379w	1380w	1380w	
					1362w	1365vw	1365vw	1362w	1365w	1364w	
1330s	1329m	1331m	1329s	1324m	1327s	1325s	1325s	1324s	1329s	1329m	1327m
								1310m, sh			
1308s	1002m	1300m	992m	1292m	1300m	1296m	992m	1290m, sh	1303m	1000m	1280m
		1252w	1232w								
1209w	945m	1209w	938m	1210w	1206w	1202m	935m	1210m	1213w	945m	1194w
				1204w				1205m, sh	1205w		
1178s		1180s	1178s	1175s	1166s	1174s	1174s	1174s	1176vs	1176m	1170s
1039m	1039m	1046s	1040s	1038w	1040m	1038m	1038m	1040m	1041m	1041m	1037m
1030m	1030m	1024s	1020s	1030w	1030m, sh	1030m	1028m	1030m, sh			1030m
979m	976m	980s	973s	978m	986m	978m	973m	979m	980m	977m	978m
963w		962m		962m	963w	962m		963w	965m	945m	963m
916m	913m	918m, sh	915s	910m	911s	910s	909m	911s	912m	912m	912m
876s	875m		890m	880m	880s	878s	876m	882s	887m	887m	865s
	859m	868m	862s	869m	868s	868s	864s	870s	878m	875m	856m
818m		800w, b					762w				
					707w						
					695w	682m					

TABLE II

OH and OD stretching frequencies in pyrone salts

	ν_{OH}	$\Delta\nu_{1/2}$*	ν_{OD}	$\Delta\nu_{1/2}$	ν_{OH}/ν_{OD}
		2,6-Dimethyl-4-pyrone salts			
Cl^-	2086	140	~1609		~1.30
Br^-	2364	172	1859	75	1.27
I^-	2695	200	2079	80	1.29
$HgCl_3^-$	2810		2153		1.31
ClO_4^-	2962		2230	160	1.33
$TiCl_6^=$	3050	215			
$ZrCl_6^=$	3100	180			
$SnBr_6^=$	3100	235	2320	110	1.34
$SnCl_6^=$	3100	200			
$PtCl_6^=$	3152	212	2350	112	1.34
$SbCl_6^-$	3310	170			
		4-Pyrone salts			
Cl^-	2128	190			
Br^-	2380	200	1880	110	1.27

*Approximate band half-widths: where none is given it could not be estimated because of overlapping of multiple bands.

TABLE III

OH and OD bending frequencies in pyrone salts

	δ_{OH}	δ_{OD}	Ratio	δ_{OH}	δ_{OD}	Ratio
			2,6-Dimethyl-4-pyrone salts			
Cl^-	1316	1010	1.30	1210		
Br^-	1307	1002	1.30	1209	948	1.28
I^-	1290	996	1.30	1203	939	1.28
$HgCl_3^-$	1308	1002	1.30	1209	945	1.28
ClO_4^-	1300	992	1.31	1209	938	1.29
$TiCl_6^=$	1294			1210		
$ZrCl_6^=$	1300			1206		
$SnBr_6^=$	1296	992	1.31	1202	935	1.29
$SnCl_6^=$	1290			1210		
$PtCl_6^=$	1303	1000	1.30	1213	945	1.28
$SbCl_6^-$	1280			1194		
			4-Pyrone salts			
Cl^-	1343	1003	1.34	1209	1058	1.14
Br^-	1339	988	1.35	1203	1052	1.14

to a hydrogen-bonded species CO···H—OH. These values of ν_{CC} and ν_{CO} fall reasonably well on a curve constructed from the values previously quoted in 2,6-dimethyl-4-pyrone complexes (1).

In the spectra of aqueous solutions of 2,6-dimethyl-4-pyrone hydrochloride, a band near 1490 cm^{-1} due to the carbonyl vibration of the protonated molecule should be observed. In aqueous solution the carbonyl proton may be hydrogen bonded, not to the Cl^- ion, as in the solid, but to the oxygen atom of a water molecule, and it would therefore be reasonable to assume a change in ν_{OH}. Such an interaction would not be expected to cause much alteration in ν_{CO} (for example, in $CHCl_3$ solution the hydrochloride has a carbonyl frequency at 1490 cm^{-1}, in almost exactly the same place as in the solid phase).

The spectra of the aqueous solutions do show the 1490 cm^{-1} band, indicating the presence of the protonated species, and this band gets more intense relative to other

TABLE IV
Bands in spectra of aqueous solutions of 2,6-dimethyl-4-pyrone and its hydrochloride

	2,6-Dimethyl-4-pyrone		2,6-Dimethyl-4-pyrone hydrochloride			
		H_2O sol.		H_2O sol.		
	Solid	2.5 *M*	Solid	1.0 *M*	2.5 *M*	5.0 *M*
ν_{CC} (H_2O)	1670vs	1660vs		1660vs	1658s	1660s
ν_{CC} (HCl)			1630vs	1645s	1642s	1642vs
ν_{CO} (H_2O)	1612vs	1582vs		1583s	1580m	1580m
ν_{CO} (HCl)			1490s	1498w	1490m	1492s
ν_{CC}	1600vs	1592s, sh				
ν_{CC}			1550s	1555m	1555s	1565s
	1432m	1430m		1430vw	1430w	1430w
δ_{CH_3}	1396s	1402s	1416m	1409w	1408m	1408m
	1372s		1382m	1375w	1370w	
δ_{CH_3}	1342m	1329m	1326s	1335m	1332m	1334m
δ_{OH}			1316s			
		1270w				
			1210w			
δ_{CH}	1200m	1194m	1179s	1192m	1190s	1190s
	1161s	1163m		1168w	1170m, sh	1166m
		1085w	1070w			
			1046w			
			973m	978w	975w	975w
	958m	948m	956m	948w	949w	950w
γ_{CH}	928m		921m			
	900s	904m	903m	908w	911m	912m
			895m			
γ_{CH}		872m	866m	872w	872m	876m

bands as the solution gets stronger. All the solutions gave spectra containing two doublets, at about 1660 and 1642 cm^{-1} and at about 1582 and 1555 cm^{-1}. Their intensities vary with the concentration. The low-frequency component of each doublet increases in intensity relative to the high-frequency one with increasing solution strength. Both these doublets are broad. The higher-frequency pair of bands is due to a C=C vibration (I) and indicates a proportion of both neutral and protonated species. The lower-frequency pair is not related, the 1582 cm^{-1} band being ν_{CO} interacting with H_2O, the 1555 cm^{-1} band being another ring mode (III). (See Table I.) This band was not confidently assigned previously (1) as in many of the complexes it was obscured by other bands.* The intensities again, though, indicate the presence of both species. The two sets of bands, together with the 1490 cm^{-1} band, show that the more dilute the solution the less the proportion of protonated material. Bands lower in frequency than 1400 cm^{-1} appear at about the same frequency in both materials.

It appears possible therefore to offer an explanation of the statement made previously that the Raman shifts in protonated and neutral molecules, *in aqueous solution*, are so similar (7, 8). In the Raman effect the OH stretching vibration produces only weak bands. The perturbed carbonyl vibration may also be expected to give rise to a weak band, since the protonated species has only C_s symmetry. For these reasons, therefore, the 2086 and 1490 cm^{-1} shifts were overlooked and the 1642 and 1555 cm^{-1} shifts regarded as due to the same vibration as in the neutral molecule. The broadness of the bands and the difficulty of exactly measuring the center also added complications.

**The spectrum of 2,6-dimethyl-4-thiopyrone contains two strong bands at 1640 and 1559 cm^{-1}. Since the* CS *stretching vibration is well removed from this region these two bands can be attributed to vibrations of type I and III respectively. In the* HBr *salt, these two bands are little changed in position at 1632 and 1528 cm^{-1}.*

It is significant that Wolkenstein and Syrkin (7) quoted a medium line at 1494 cm^{-1} in the aqueous solution of 2,6-dimethyl-4-pyrone hydrochloride, while the neutral molecule in aqueous solution had a very weak line at 1493 cm^{-1}. Kahovec and Kohlrausch (8) did not observe this line. The former authors used a solution approximately 2.3 M in the salt whereas the German authors used a solution of about 0.4 M (2 g hydrochloride in 5 ml H_2O).

4-Pyrone Salts

The bands in the spectra of 4-pyrone salts are shown in Table I; the OH stretching vibrations occur in positions similar to those of the 2,6-dimethyl-4-pyrone salts and show similar movements on deuteration (see also Table II). The in-plane hydrogen-deformation frequencies are close to 1340 cm^{-1} and, as for the 2,6-dimethyl-4-pyrone salts, are accompanied by a lower-frequency band near 1200 cm^{-1} (see Table III). On deuteration both bands disappear to be replaced by two new bands near 1050 and 1000 cm^{-1}. The ratios $1340/1050 = 1.28$ and $1200/1000 = 1.20$ indicate that mechanical effects may have some role in the value of the lower frequency. If the alternative ratios are considered, $1340/1000 = 1.34$ and $1200/1050 = 1.14$, then the higher-frequency band behaves normally, but the low ratio for the 1200 cm^{-1} band is difficult to understand.

The carbonyl vibration in the 4-pyrone salts also comes close to 1490 cm^{-1} and the C=C stretching vibration (I) moves to lower values in the salts, 1610 cm^{-1} compared with 1660 cm^{-1} in the neutral pyrone. The existence of some mechanical interaction between these two vibrations in the neutral pyrone, as proposed by Phillips (10), is therefore confirmed. These similarities between 4-pyrone and 2,6-dimethyl-4-pyrone are reasonable, and to be expected, as the replacement of a hydrogen atom by a methyl group is not expected to result in large changes in the properties of the carbonyl group, or its ability to protonate.

A few weak bands have been noticed in the 4-pyrone deuterated salts that have no analogue in the normal salts. These were at 1528, 1320, and 1229 cm^{-1} in the DCl salt, and at 1530, 1318, and 1226 cm^{-1} in the DBr salt. These must be attributed to combination tones or overtones of some band or bands associated with a low-frequency vibration involving the OD group. Strong bands in the 4-pyrone salts at 1185, 941, and 848 cm^{-1} could be combined with low-frequency vibrations at about 368 and 290 cm^{-1}, giving the following possible summation tones: $1185+368 = 1553$ (1530); $941+368 = 1309$ (1320); $941+290 = 1231$ (1230); $848+368 = 1216$ (1230). In the absence of a study of the deuterated molecules in the low-frequency region little progress can be made with these assignments. The possibility that exchange occurred between the ring protons and the deuterium in the acid is present, but is considered small since no indication of CD stretching absorption bands was noted.

In support of the assignments made for γ-pyrone salts the spectra of many 4-pyridone salts show almost identical features (14). The proton stretching bands occur in the same region and move to higher frequencies as the anion gets larger. The in-plane hydrogen-deformation vibration is near 1300 cm^{-1} (and is also doubled), moving close to 1000 cm^{-1} on deuteration. This is so similar to the 4-pyrone series that a similar structure, i.e. protonated at the carbonyl group, is suggested. Nuclear magnetic resonance experiments have been interpreted as being consistent with this view (15). N-Protonation can be rejected on a further count; such a structure would be similar to tertiary amine salts, which have bending modes near 1400 cm^{-1}, for example, trimethylamine salts,

$1420\ cm^{-1}$ (16, 17); N-alkylpiperidine salts, $1400\ cm^{-1}$ (14); triphenylamine salts, 1390 cm^{-1} (17). The absence of a band near $1400\ cm^{-1}$ with the appropriate shift on deuteration is strong evidence against N-protonation.

EXPERIMENTAL

The Spectra

A Perkin–Elmer model 221 prism-grating spectrometer was used to record the spectra. Solid-state spectra were of emulsions of the finely ground solid in nujol and fluorolube. Aqueous solution spectra were of thin films trapped between Irtran plates. Difference spectra were obtained by inserting a thin film of water between Irtran plates in the reference beam. A trial and error method of exact compensation was used by varying the pressure on the plates. While small differences in intensity were noted in various spectra no shifts in position in bands below about $1700\ cm^{-1}$ were observed. The water bands in the 3-μ region varied considerably, but have not been used for diagnostic purposes.

2,6-Dimethyl-4-pyrone Salts

2,6-Dimethyl-4-pyrone was prepared from dehydroacetic acid by boiling with concentrated HCl followed by evaporation of the liquid to give the hydrated HCl salt. This was then recrystallized from pyridine to give the pyrone, which was then recrystallized from methanol. M.p. 131–133°.

Hydrochloride.—1 g 2,6-dimethyl-4-pyrone in 10 ml $CHCl_3$ and 50 ml ether when treated with anhydrous HCl gave a copious precipitate of the salt. M.p. 153–155°. This was used without further treatment. Due to its hygroscopic nature and ready hydration to the dihydrate it was handled in a dry box. To prepare the DCl salt a CCl_4 solution of the anhydrous pyrone was treated with excess DCl in a vacuum system. The excess DCl and all solvent were removed by evacuation, the solid being subsequently handled in a dry box.

Hydrobromide.—Exactly the same techniques as for the HCl salt were used. M.p. 192–193°. DBr was used to make the deuterated salt.

Hexabromostannate.—The hydrobromide was prepared as above, and redissolved in $CHCl_3$. Excess $SnBr_4$ then precipitated a white deposit of the hexabromostannate. M.p. 195–197°.

Hexachlorostannate.—Same procedure using $SnCl_4$. M.p. 210–213°.

Hexachlorotitanate.—Same procedure using $TiCl_4$. Dry box handling was necessary.

Hexachloroplatinate.—1.24 g 2,6-dimethyl-4-pyrone was dissolved in 20 g 10% aqueous $H_2PtCl_6.6H_2O$. After 4 days light brown crystals started forming. M.p. 188–190°. The deuterated material was made by twice exchanging with a 100-fold excess of D_2O and removing the excess D_2O *in vacuo.*

Hexachloroantimonate.—The procedure for the hexabromostannate was followed but with HCl and $SbCl_5$. M.p. 92–94°.

Hydroiodide.—Aqueous HI was shaken with ether, the ethereal layer after separation being added to a solution of the pyrone in a little $CHCl_3$ and excess ether. The pale yellow solid so formed was used without further purification. M.p. 176–179°.

Perchlorate.—1.68 g aqueous 70% perchloric acid was added to 1.24 g pyrone in 3 ml H_2O, and excess H_2O removed *in vacuo.* M.p. 78–80°.

Trichloromercurate.—An acetone solution of the pyrone:$HgCl_2$ complex was treated with dry HCl gas, and a deposit of the solid was found when the excess solvent was removed on a vacuum line. M.p. 118–120°.

Hexachlorozirconate.—A solution of the pyrone.HCl in $CHCl_3$ was added to a $CHCl_3$ solution of $ZrCl_4$, giving a white precipitate of the complex salt. M.p. 257–259°.

Aqueous Solutions

Aqueous solutions of 2,6-dimethyl-4-pyrone hydrochloride were prepared from the dihydrate. Solutions 1.0, 2.5, and 5.0 *M* were used. The solution of the pyrone in water was 2.5 *M.*

4-Pyrone Salts

4-Pyrone was prepared by the decarboxylation of chelidonic acid by heating with copper powder to about 300° C.

Hydrochloride.—Dry HCl gas was passed into a solution of pyrone in $CHCl_3$ and ether. The white solid so formed, m.p. 132–134°, was used without further treatment, and due to its hygroscopic nature, handled in a dry box. The deuterated salt was prepared from a CCl_4 solution of the pyrone and DCl using a high-vacuum apparatus. The excess fluid was decanted, leaving a white solid which was subsequently handled in a dry box. Attempts to remove solvent by evacuation resulted in decomposition of the solid.

Hydrobromide.—The pyrone in a little $CHCl_3$ and excess ether when treated with HBr gas gave a white solid. An indeterminate melting point was observed with charring between 150° and 180°. The DBr salt was obtained from a benzene solution of the pyrone though not with complete isotopic exchange. All deuterated salts were made by exchange with excess D_2O unless otherwise stated. Melting points were taken in sealed capillary tubes and are uncorrected.

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