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ABSORPTIONS OF CYCLOPROPANONE IN THE INFRARED CARBONYL REGION

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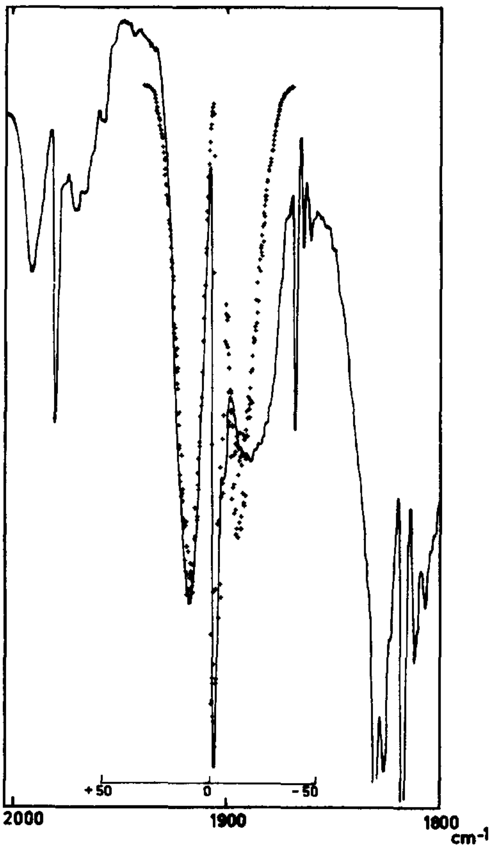
Conflicting interpretations[3-8] as to the origin of the low infrared carbonyl frequency of (dissolved[9]) cyclopropanone are found in the literature. Current confusion on this subject can be traced back to a "missing link": the exact value of the vapour-phase carbonyl frequency. The only reported[10] vapour-phase frequency of 1815 cm^{-1} is clearly incorrect, and must be ascribed to cyclobutanone (vide infra). Therefore, it seemed important to reappraise the infrared spectrum of cyclopropanone.

For the vapour-phase measurements[11], cyclopropanone, prepared from ketene and diazomethane, was – after removal of the twenty-fold excess of ketene – distilled from di-n-butyl ether into the evacuated infrared gas cell. As cyclopropanone is known to be extremely reactive towards all types of nucleophiles[12], this procedure unavoidably leads to loss of cyclopropanone and, therefore, to a relative increase in the concentration of volatile contaminants present. Thus, our study had to be limited to the carbonyl region (1700-2000 cm^{-1}), since other spectral regions are obscured by bands arising from the known contaminants (i.e. the observed bands at 1450, 1370, 1260, 1010 and 910 cm^{-1}, coincide with bands of 1,1-dihydroxycyclopropane or polycyclopropanone[13], those at 3060, 3010, 2980, 2940, 1225 and 950 cm^{-1} with absorptions of cyclobutanone and those at 3080 and 1130 cm^{-1} with ketene frequencies).



INFRARED SPECTRUM OF CYCLOPROPANONE

—— vapour phase spectrum

+++++ computed A-type rotational-vibrational band;

rotation constants used:
$A'' = 0.67116$, $A' = 0.65774$ cm^{-1}
$B'' = B' = 0.24862$ cm^{-1}
$C'' = C' = 0.19557$ cm^{-1}
Temperature 300°K

In the carbonyl region (see fig.) four absorption bands are observed: 1980 (s); 1905.6 (v s); 1867 (m) and 1815.6 cm^{-1} (v s). The band at 1815.6 cm^{-1} is ascribed to cyclobutanone for the following reasons: (a) it exactly coincides with the vapour-phase frequency of cyclobutanone, and (b) the intensity of the 1816 cm^{-1} band does not change with time, whereas the other three bands become gradually weaker as a result of the reaction of cyclopropanone with traces of nucleophiles. Complete disappearance of the three other bands can be effected by reaction with gaseous methanol (giving 1-methoxycyclopropanol) or with diazomethane. The product of the latter reaction is cyclobutanone[14] and consequently the intensity of the 1816 cm^{-1} band increases. The remaining three bands observed in the carbonyl region must therefore be ascribed to cyclopropanone. Further evidence has been obtained by computing the theoretical band envelope, using the ground state rotational constants reported by Pochan et al[15]. A fitting calculated spectrum (see fig.) has been obtained by varying the A" rotational constant from 0.67116 cm^{-1} (ground state[15]) to A' = 0.6577 ± 0.002 cm^{-1} (excited state). The extremely large difference[16] between A" and A' affords additional support for the proposed[15] weakness of the C_2-C_3 bond in cyclopropanone. The C_2-C_3 bond length (1.57 Å, ground state) of cyclopropanone in the vibrational excited state is estimated to be 1.61 Å.

On the basis of the above evidence, together with the relative intensity of the observed bands, we are now able to ascribe the 1906 cm^{-1} vapour-phase absorption band unequivocally to the carbonyl absorption of cyclopropanone.

The three bands observed in the vapour-phase spectrum are also found for dissolved cyclopropanone, although two bands are shifted to lower wave numbers by about 80 cm^{-1}, i.e. the 1980 cm^{-1} band (vapour, s) shifts to 1908.5 cm^{-1} ($CHCl_3$,s) and the strongest band at 1905.6 cm^{-1} (vapour) to 1822.1 cm^{-1} ($CHCl_3$, v s). The frequency of the band at 1867 cm^{-1} (vapour, m) remains almost unaffected in solution (1870 cm^{-1}, $CHCl_3$, vw) and – in view of its weakness – may well be due to an overtone or combination band.

The 1980 cm^{-1} band cannot originate from a hot-band type effect. The relatively high intensity (borrowed from $\nu_{C=O}$?) of the absorption at 1980 cm^{-1}, together with its shift to much lower frequencies on going from the vapour phase to solution suggests a high degree of carbonyl character.

This Fermi-resonance[17] should then originate from two different overtone or combination bands (one at about 1960 cm^{-1} in the vapour phase and another at about 1860 cm^{-1} in solution). A more detailed discussion, especially concerning the spectral behaviour of cyclopropanone in solution, will be given elsewhere.

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