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INFRA-RED SPECTRA OF HALOGENOALKANES. A NEW CORRELATION

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Summary. Halogenoalkanes exhibit intense infra-red absorption bands in the region 1140-1320 cm^{-1}, which can be of diagnostic value and should be included, along with the characteristic C-halogen stretching frequencies, in spectral correlation tables.

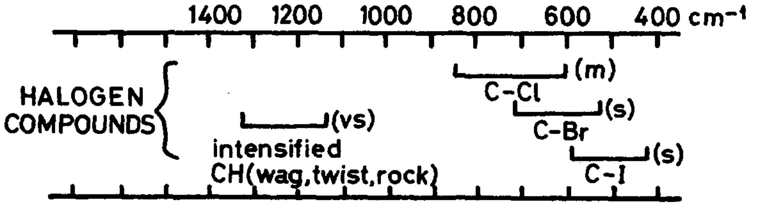
Without exception, the standard texts on infra-red correlations of organic molecules include a statement, or implication, to the effect that the only characteristic absorption in the infra-red spectra of halogenoalkanes is that associated with the carbon-halogen stretching mode.[1] Unfortunately, this is of little value for routine diagnosis of bromo- and iodoalkanes since their C-halogen stretching frequencies fall outside the range of routine infra-red spectrometers.[2] However, we now report that intense bands in the region 1140-1320 cm^{-1} can be of diagnostic value for these compounds. Indeed, our recent experience indicates that the omission of these bands from correlation tables can be positively misleading.

In connection with other work, one of us obtained an unexpected reaction product which had an i.r. spectrum (4000-650 cm^{-1}) resembling that of an alkane, except that there was considerable intensification of features at 1210 and 1170 cm^{-1}, which were almost the strongest in the spectrum. Consultation of standard correlation tables[1] gave no indication of the appearance of strong bands in this region for the class of compound to which the product was subsequently shown to belong, viz: an iodoalkane. This caused some delay in our identification of this compound. As a result, we undertook a correlation study of halogenoalkanes, utilising spectra from the literature, including the DMS collection, and several from our own spectral files.

For mono- and di-iodoalkanes we consistently observed one or more very intense bands in the region 1140 to 1320 cm^{-1} (in many cases the most intense in the spectrum). A similar pattern, but shifted to somewhat higher frequency - usually between 1200 and 1320 cm^{-1} - was seen in the mono- and dibromoalkanes, often with a multiplicity of bands in the latter cases. Although a similar pattern, again shifted to somewhat higher frequencies (ca. 1230-1320 cm^{-1}) appears for the chloroalkanes, the situation is somewhat less clear cut. We have not investigated fluoroalkanes in the light of the presence of the C-F stretching mode, which is itself characteristic, in this region.

The bands in the region 1140-1320 cm^{-1} arise from the hydrocarbon framework of the halogenoalkanes, and are due to coupled motions involving CH_2 wagging, twisting, and rocking, with possible contributions from C-C skeletal vibrations. Such bands in alkanes are usually weak, and have not proved very amenable to correlation studies. The presence of a halogen atom evidently brings about considerable intensification of some of these modes. For those compounds which have spectra which are otherwise alkane-like, especially iodoalkanes and to a lesser extent bromoalkanes, these bands can clearly be of diagnostic value.

The observation that the presence of a polar group causes intensification of hydrocarbon modes has been commented upon briefly by Bellamy[3] and by Nakanishi[4] in their discussions of the spectra of alkanes. The bands have been thought, however, to be of little diagnostic value, and halogenoalkanes were not specifically considered. Our present correlations show that this is not the case. Very intense bands in the region 1140-1320 cm^{-1} may indeed be indicative of a halogenoalkane. The omission of a statement to this effect may be misleading, and as such these bands should be listed in correlation tables, along with C-halogen stretching frequencies. We would suggest an addition to correlation tables as follows:



References and Notes

1. See for example: (a) L.J.Bellamy, "The Infra-red Spectra of Complex Molecules", 3rd edition, Chapman and Hall, London 1975; (b) K.Nakanishi, "Infra-red Absorption Spectroscopy" Holden-Day, San Francisco, 1962; (c) F.Scheinmann, "An Introduction to Spectroscopic Methods for the Identification of Organic Compounds", Volume 1, Pergamon, Oxford, 1970; (d) M.St.C.Flett, "Characteristic Frequencies of Chemical Groups in the Infra-Red", Elsevier, Amsterdam, 1963; (e) I.Fleming and D.H.Williams, "Spectroscopic Methods in Organic Chemistry", McGraw-Hill, London, 1966.
2. F.F.Bentley, N.T.McDevitt, and A.L.Rozek, *Spectrochim.Acta*, 1964, **20**, 105; and references cited therein.
3. L.J.Bellamy, "Advances in Infrared Group Frequencies", Methuen, London, 1968, p.15; see also ref. 1(a), p.28.
4. Ref. 1(b), p.22.