Nuclear Magnetic Resonance Studies of Boron Trifluoride Complex Formation

HIGH-resolution nuclear magnetic resonance spectroscopy affords a uniquely penetrating method of studying co-ordinate complex formation between boron trifluoride and electron donor substances. The examples investigated so far comprise oxygen compounds (water, alcohols, ethers and ketones), but the method promises wide application. Details of a typical experiment follow. Fluorine magnetic resonance (at a frequency of 34·2 Mc./s.) is observed in a quantitatively prepared liquid mixture of two donor substances (as, say, methanol and ethanol) with boron trifluoride, the latter in quantity insufficient to saturate both donors. The temperature is controlled during a given measurement, the usable range extending from somewhat above room temperature to about − 100° C. At sufficiently low temperatures two relatively narrow resonance peaks are seen, separated in the case cited by some 70 c./s. These correspond to the co-ordination complexes of the respective donors. Measurement of the peak areas (assumed to be proportional to the volume concentrations) in mixtures of various composition indicates that reversible equilibrium is established between the two donors and their respective complexes. The mass law constant may thus be measured. The values at a series of different temperatures yield the corresponding enthalpy and standard entropy changes for the interconversion reaction.

Such an equilibrium constant is the ratio of the mass law constants for the dissociation of the respective complexes into boron trifluoride and donor substance. A properly chosen series of studies with pairs of donors allows establishment of a 'boron trifluoride affinity' series; as an example, at a given temperature the substances water, methanol, ethanol, *n*-propanol and *n*-butanol constitute a regular series, the water – boron trifluoride complex displaying the greatest stability. Mixtures containing three or more donor substances also demonstrate the order in such a series. Of particular interest is the comparison of isomeric substances, in which cases rather remarkable differences in boron trifluoride affinity are often observed.

As the temperature of such a mixture as that cited above is raised, the two fluorine resonance lines are observed to broaden and ultimately to merge. This behaviour is typical of chemical exchange effects, as already observed in previous studies by one of us (R. A. O.)[1].

In qualitative terms, the line broadening occurs as the pseudo-monomolecular rate constant for the interconversion approaches in value the frequency separation of the lines. Systematic studies allow the evaluation of the rate constants at various temperatures, yielding the corresponding activation energies.

The equilibrium and kinetic studies indicated above are possible because of the rather striking variation of the fluorine resonance position ('chemical shift') as the donor substance is altered. The careful measurement of these chemical shifts, and their relation to structure and other properties of the co-ordination complexes, constitute another aspect of the entire programme. Of no less interest is the observation and interpretation of proton resonances. As an example, the formation of the boron trifluoride complex of ethanol results in a marked displacement (more than 100 c./s. as compared with pure ethanol) of the hydroxyl proton resonance toward lower magnetic field. The shift of the methylene resonance is in the same sense, but considerably smaller, while that of the methyl group resonance is negligible.

An extended programme of studies is in progress with the aim of following in systematic fashion the dependence of the various measurable quantities upon the molecular structure of the donor substances.

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Absorption Spectra of Flat Flames using a Multiple-Reflexion Technique

MANY previous attempts to detect absorption bands of intermediate oxidation or pyrolysis products in premixed (Bunsen-type) flames have failed. There are several difficulties in studying absorption spectra of flames; the reaction zone where intermediate products may be expected is usually extremely thin and often curved; it is necessary to have a background source the brightness of which exceeds that corresponding to the effective excitation temperature in the flame (which may sometimes be higher than the equilibrium flame temperature); the light beam may be thrown out of the flame by refraction effects; and the concentration of the absorbing species may be low because of their instability or reactivity at high temperatures, thus necessitating long path-length for their detection. To study a thin reaction zone, even if flat, it is necessary to restrict the light to a narrow beam of very small angular aperture.

We have recently made some progress in overcoming the difficulties by using (*a*) flat near-limit flames, of the type developed by Egerton and Powling[1], having a reaction zone which may be a few millimetres thick and fairly flat, (*b*) a very bright xenon high-pressure lamp ('Osram' type *XBO*.162) as background source, and (*c*) a system of mirrors, of the type employed by White[2], to reflect the beam of light backwards and forwards a number of times through the flame gases.

We have designed a metal flat-flame burner with a rectangular matrix, giving a flame about 8 cm. long. The burner has side-tubes containing the mirror system, with quartz windows for viewing. Front-surface aluminized mirrors were found to tarnish when exposed to some types of flame, and we have therefore used back-surface aluminized mirrors made from quartz, with the curvature of the surfaces so designed that images formed by reflexion from the front and back surfaces coincide.

Gradients of refractive index in the flame gases are low under our experimental conditions, and have not caused appreciable defocusing with less than twenty traverses.

Exposures of usable intensity on a medium quartz spectrograph have been obtained in 30 min., with twenty-four traverses in the region of 2500 A., and in 10 min., with thirty-six traverses in the visible region. With fewer traverses than those just quoted, it is possible to increase the spatial resolution in the flame gases by stopping down the vertical aperture. Good quartz/lithium fluoride achromat lenses have been used for ensuring good focus in the near ultra-violet as well as the visible.

Flames of diethyl ether with air show a weak cool flame below the main blue-flame front, near the rich limit. Under carbon-forming conditions, there is a dark zone between the main blue-flame front and the yellow carbon zone, and the gap separating the cool flame from the main flame is barely discernible; the carbon zone appears for only a relatively narrow range of mixture strengths, disappearing for the richest mixtures. For these ether flames we have found clear, strong absorption bands of formaldehyde (3500–2600 A.) which are strongest in the region between the cool and main flames. Under carbon-forming conditions and with a path-length of nearly 200 cm., benzene absorption bands have been found (λλ 2589, 2528 A.). The absorption bands of formaldehyde have also been detected in flames of acetaldehyde and methanol with air; the latter did not show a discernible cool flame. The hexane/air flame shows the benzene bands much more clearly than the ether flame; also an unidentified band of intensity comparable with the benzene system has been observed at about 2750 A. The bands first occur in the preheating zone well below the main flame front and persist through to the carbon zone. They do not, however, show any marked increase in intensity towards the carbon zone. Some continuous absorption is also observed in the short-wave ultra-violet in the dark space between the main flame front and the carbon zone, but no formaldehyde has been detected. For this work, the hexane was carefully freed from contaminating benzene. A trace of benzene absorption has been found in flames of methane and propane, but has not finally been confirmed.

Formaldehyde has previously been detected by Egerton and Pidgeon[3] in the slow combustion of hydrocarbons, and its occurrence in ether flames is not unexpected. The new observation of benzene is more interesting and could be used as an argument to support a theory of ring closure as a stage in carbon formation, rather than one depending on breakdown of acetylene to carbon. Processes of carbon formation have been discussed by Street and Thomas[4] and Gaydon[5]. The presence of benzene and weakness of formaldehyde in the hexane flame suggest that, in premixed flames of hydrocarbons, formation of pyrolysis products is more rapid than that of partial oxidation products. Recent work[6] on benzene absorption at high temperatures shows a loss of structure; the banded absorption observed by us probably comes, therefore, from the cooler parts of the flame, and the continuous absorption in the dark space of the hexane flame may also be caused, at least in part, by benzene.

For explosion flames of carbon monoxide, Knipe and Gordon[7] have given some evidence that part of the structure of the carbon monoxide flame bands may be due to absorption, possibly by carbon monoxide molecules in the $a^3\Pi$ state. We have looked for both the triplet and third positive systems of carbon monoxide in absorption, using up to thirty traverses through a rich-limit flame of undried carbon monoxide, but have seen no signs of them.

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Low-angle X-ray Observations on Glass

VARIOUS low-angle X-ray scattering effects from some glasses have been reported by Hoffman and Statton[1]. Essentially the same experiment has been carried out on similarly heat-treated silica-glass plates using monochromatic X-radiation, and no low-angle diffraction effects of any sort have been observed. A possible explanation of the observations of Hoffman and Statton is considered here.

Lu and Chang[2] also observed some low-angle diffraction effects from glasses, which were explained by Rooksby and Thomas[3] as due to the very short wave-lengths of the white radiation present in the nickel-filtered X-ray beam used. The same effect appears to be operative in the experiments of Hoffman and Statton. This has been confirmed by taking a photograph of a silica plate, first with crystal-reflected monochromatic copper K_α radiation, and then with nickel filtered copper K_α radiation. A low-angle diffraction ring is observed with the nickel-filtered radiation (Fig. 1).

The position of the low-angle ring will depend on the peak voltage of the X-ray tube used. At high tube-voltages, the band will move into the backstop and appear as diffuse low-angle scattering. This would account for the different behaviour of quenched and annealed samples of silica glass and of a

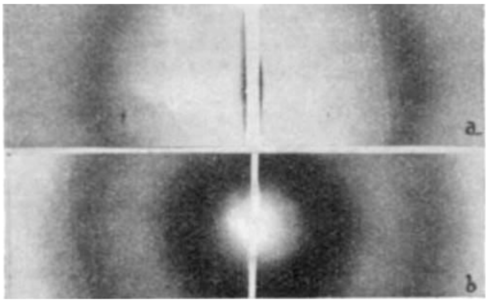

Fig. 1. X-ray photographs of a silica plate, 0·18 mm. thick, using (*a*) monochromatic copper $K\alpha$ radiation, by reflexion from a lithium fluoride crystal. The photograph was taken in vacuum, in a focusing camera, 7 cm. in diameter; (*b*) nickel-filtered radiation. Photograph taken in air, on a flat plate, 7·5 cm. from specimen. The peak voltage of the X-ray tube was 35 kV., and the nickel foil was 0·001 in. thick. In the case of the nickel-filtered radiation, a low wave-length component of the white radiation remains, which produces the low-angle inner ring