The $N_2F_4 \rightleftharpoons 2NF_2$ Equilibrium studied with a Tunable Infrared Diode Laser

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The enthalpy change for the $N_2F_4 \rightleftharpoons 2NF_2$ equilibrium has been determined at temperatures between 50 and 200 °C and pressures between 5 and 26 Torr using an infrared diode laser to measure relative NF_2 concentrations; using lines in the ν_1 band of NF_2 to determine intensities and allowing for the finite degree of dissociation at the pressures used, a value for ΔH of 78 ± 6 kJ mol^{-1} was calculated, in good agreement with previous determinations.

The equilibrium between tetrafluorohydrazine and difluoroamino radicals is one of the few examples of a gaseous molecule–radical equilibrium at near room temperature.[1] The enthalpy of dissociation has been determined by measuring the pressure variation as a function of temperature at constant volume,[1] and spectroscopically by u.v. spectrophotometry[1] and e.s.r. techniques.[2] Although the i.r. spectra of N_2F_4[3] and NF_2[4,5] have been known for some time and i.r. spectroscopy has been widely used for studying gaseous equilibria, the method does not appear to have been applied to the $N_2F_4 \rightleftharpoons 2NF_2$ equilibrium. This is due in part to the relatively weak i.r. spectra of NF_2 even at high concentrations which makes accurate measurement of intensities difficult.

Recently we have been using a tunable i.r. diode laser to record spectra of NF_2[6] (and other radicals and transients[7–11]) at Doppler-limited resolution with signal to noise ratios much higher than with conventional grating spectrometers. We have now measured the enthalpy of dissociation of N_2F_4 from the diode laser spectra of NF_2, not only to provide a new determination of ΔH but also as a means of assessing this form of spectroscopy for thermodynamic measurements of this kind. The experimental arrangement consisted of a Laser Analytics Inc. LS-3 spectrometer and a 10 cm absorption cell which could be heated up to 200 °C. Measurements were made on the ν_1 band of NF_2 (symmetric stretch) near 1100 cm^{-1}. This region had been studied earlier[6] and is free of N_2F_4 spectra. The ν_1 band appeared as a perpendicular band of a near symmetric top with readily identifiable Q-branches, away from the band centre.[4] At the resolution of the diode laser each line appeared as a doublet owing to interaction of the single unpaired electron with rotational motion.[6]

Figure 1 shows part of the spectrum as the temperature was varied. At the pressures used in these experiments pressure broadening is likely to make a significant contribution to linewidth and experiments with stable gases confirmed this. Therefore to determine relative concentrations of NF_2 integrated line intensities rather than peak amplitudes were used. Another factor which might contribute to linewidth, power broadening, is entirely negligible at the diode laser power available (<1 mW). Integrated intensities, I, were then used to determine ΔE from equation (1) where the term in α

$$\log_{10} I + \log_{10}[\alpha/(1-\alpha)] = -\Delta E/(2.303RT) + \text{const.} \quad (1)$$

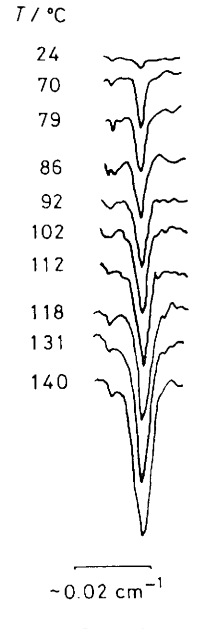

Figure 1. One component of a spin rotation doublet, from the diode laser spectra of NF_2, near 1104 cm^{-1}, increasing in intensity with temperature.

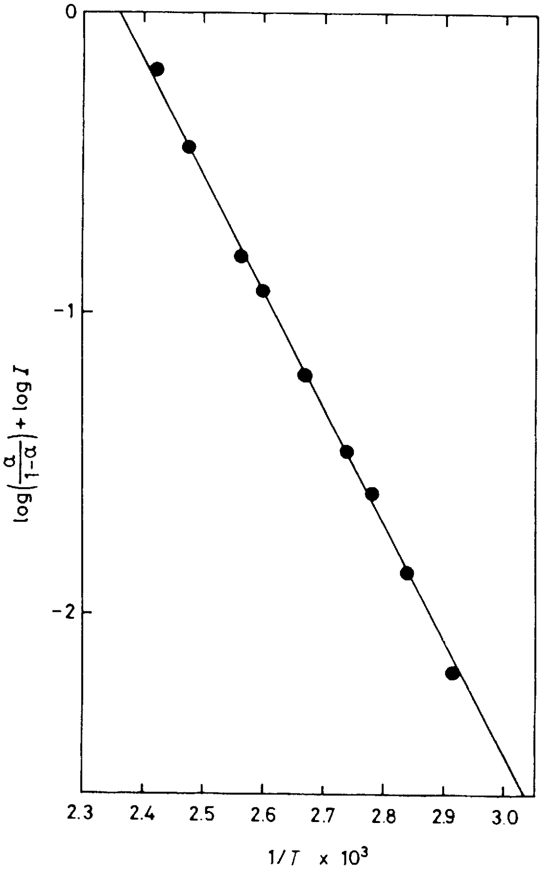

Figure 2. Intensity of NF_2 diode laser signals plotted according to equation (1).

allows for the finite degree of dissociation of N_2F_4 at the pressures used. Values of α for each temperature were calculated from the earlier equilibrium measurements of Johnson and Colburn.[1] A plot of the data using equation (1) and a pressure of 9.7 Torr of N_2F_4 (298 K) is shown in Figure 2 yielding $\Delta E = 75.2 \pm 4$ kJ mol^{-1}. The average result gave $\Delta H = 78 \pm 6$ kJ mol^{-1} (from $\Delta H = \Delta E + \Delta n\, RT$, $\Delta n = 1$).

No significant difference was detected between different spin components and the result is in good agreement with previous work.[1,2] Both spectroscopic methods employed earlier also monitored NF_2 absorption. It is concluded that the use of diode laser spectroscopy, with high resolution and sensitivity, has considerable potential for the measurement of enthalpies of dissociation and isomerisation.

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