Short Communications

Temperature Effect on the Absorption Spectrum of Cyclooctatetraene

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Pink and Ubbelohde [1] have recently reported that the yellow colour exhibited by cyclooctatetraene at ordinary temperatures more or less disappears in the neighbourhood of the boiling point of liquid oxygen, but reappears reversibly at rising temperatures. In the course of investigations of cyclooctatetraene carried out in this laboratory we have independently noticed a marked change in colour with temperature. In order to verify this visual observation we have measured the absorption of pure cyclooctatetraene quantitatively in the visible spectrum at different temperatures.

A Beckmann spectrophotometer was used for the measurements. The cyclooctatetraene was filled into a 1 cm cell which could be electrically heated, the temperature being controlled by means of a thermocouple. Care was taken to exclude the atmospheric oxygen from the sample. The absorption was measured in the region 4600—5600 Å at three different temperatures, *viz.* 25, 58 and 90° C. The results for the two higher temperatures were corrected for thermal expansion. In Fig. 1 the found log ε (in arbitrary units) are plotted against the wave numbers. It will be seen that there is a marked increase

in absorption with rising temperature. Our experiments have shown that this change is reversible.

Theoretically such an increase should be expected because the long-wave end of the absorption spectrum is due to transitions from thermically excited vibrational levels of the molecule in its electronic ground state. At rising temperatures the population in these levels is increasing and hence an increasing absorption in this region will occur.

As a crude approximation the distribution of molecules in the different vibrational states may be assumed to be classical and the transition probability to be constant. On this basis one gets:

$$\varepsilon = \text{Const.} \int_{\nu_1 = \nu_0 - \nu}^{\infty} \frac{e^{-h\nu_1/kT}}{\int_0^{\infty} e^{-h\nu_1/kT} d\nu_1} d\nu_1$$

$$= \text{Const.}\, e^{-h(\nu_0 - \nu)/kT} \qquad (1)$$

where ν is the frequency of the absorbed light, ν_0 the frequency of the $0 \to 0$ transition and ν_2 the vibrational frequency of the molecule in its electronic ground state. This gives

$$\log \varepsilon = \text{Const.} + \frac{0.4343h}{kT} (\nu - \nu_0) \qquad (2)$$

According to this, the difference in log ε ($= \varDelta \log \varepsilon$) for two different temperatures (T_1 and T_2) should be
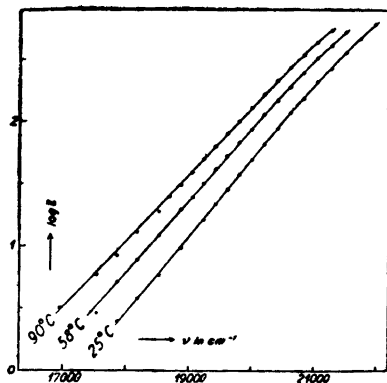
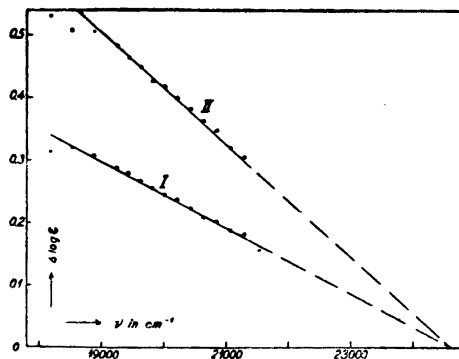Fig. 1. The long-wave end of the absorption spectrum of cyclooctatetraene at different temperatures.

Fig. 2. $\Delta \log \varepsilon$ (see text) for cyclooctatetraene. Curve I: $\Delta T = 58 - 15°C$ and curve II: $\Delta T = 90 - 25°C$.

$$\Delta \log \varepsilon = \frac{0.4343h}{k} \times \frac{T_1 - T_2}{T_1 \, T_2} (\nu - \nu_0) \quad (3)$$

By plotting $\Delta \log \varepsilon$ against wave number one should get straight lines with increasing slope for increasing temperatur intervals. Furthermore, all these lines should pass through ν_0 (i. e. the 0 → 0 frequency of the absorption band system) for $\Delta \log \varepsilon = 0$.

Fig. 2 shows the results found for cyclooctatetraene. Curve I represents $\Delta \log \varepsilon$ for $\Delta T = 58 - 25°$ C and curve II for $90 - 25°$ C. It will be seen that the measured points fall on straight lines passing through the same point ($\nu = 24600$ cm^{-1}) on the axis corresponding to $\Delta \log \varepsilon = 0$. According to the theory this should be the 0 → 0 frequency of the absorption system. However, the slopes of the lines agree badly with the values computed from equation (3):

	Slopes computed	(in 10^{-3} cm) found
I 58 — 25° C	0.21	0.05
II 90 — 25° C	0.37	0.09

The reason for this bad agreement may be the very crude approximations in the theoretical considerations given above and may also be caused by impurities in the cyclooctatetrene.

We are continuing the investigations with more suitable substances in order to see if this method can be used to an approximate localization of the 0 → 0 frequency for more or less continuous absorption spectra.

However, our preliminary measurements of cyclooctatetraene show that the visually observed change in colour with temperature is real and may be explained as an effect which generally should be found for the long-wave end of all absorption spectra. Therefore it seems unnecessary to assume the presence of a small amount of a biradical form of cyclooctatetraene, as proposed by Pink and Ubbelohde [1], in order to explain the phenomenon.

1. Pink, R. C., and Ubbelohde, A. R. Trans. Faraday Soc. 44 (1948) 708; cf. Scott, D. W., Gross, M. E., Oliver, G. D., and Hufman, H. M. J. Am. Chem. Soc. 71 (1949) 1634.