

121. Theoretical Temperature-dependence of the Rate of Isomerization of Cyclopropane.

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The theoretical temperature-dependence of the first-order rate constant for the isomerization of cyclopropane is estimated for the quantum harmonic oscillator model of unimolecular reactions. The results are in significant disagreement with Falconer, Hunter, and Trotman-Dickenson's experimental results,¹ and a tentative modification of the theoretical formula is suggested.

CONCURRENTLY with an accurate determination² of the pressure-dependence of the first-order rate constant for the isomerization of cyclopropane to propene, a theoretical calculation was made and was found³ to give good agreement over the wide range of pressure of the experiments. The calculation was based on the author's "harmonic oscillator" theory of unimolecular reactions and on classical mechanics. Subsequently this theory has been put into a quantum version,⁴ which makes little change in the form of the pressure-dependence but departs from the Arrhenius form of temperature-dependence of the high-pressure rate constant. (There is a similar, but less conspicuous, effect when in activated complex theory one passes from classical to quantum partition functions.) The new experiments by Falconer *et al.*¹ give the cyclopropane rate constant at one effectively high pressure over a wide range of temperature, and so are useful for theoretical comparisons. These new experimental results lie much closer to an Arrhenius form than do the theoretical results for the quantum oscillator theory. The purpose of this paper is to explain briefly the theoretical calculations, and to indicate a pragmatic adjustment of the theoretical form which would resolve the discrepancy.

In the quantum oscillator theory, the (high-pressure) first-order rate constant at absolute temperature T is

$$k = \nu \exp(-q^2/2\sigma^2) \text{ sec.}^{-1} \quad (1)$$

where

$$\sigma^2 = \frac{1}{4} h \sum_{i=1}^n \alpha_i^2 \nu_i \coth(h\nu_i/2kT) \quad (2)$$

with ν_1, \dots, ν_n the normal vibration frequencies of the molecule, and ν^2 a mean square frequency obtained by dividing the expression (2) into a similar sum with ν_i replaced by ν_i^3 . The rate (1) represents the mean probability per second for molecules to dissociate (or isomerize), on the assumption that this requires a particular internal dimension q_1 to reach a critically high value q . The constants α_i arise in the expression $\sum \alpha_i Q_i$ for q_1 as a sum of normal co-ordinates Q_i , which are treated as quantum oscillators of frequencies ν_i ; σ^2 is the mean square of this sum for an assembly at temperature T . The limiting form of equation (1) at high temperature is the Arrhenius form $\nu \exp(-E/kT)$ with $E = q^2/\sum \alpha_i^2$; this is also the general classical-mechanical result.

To apply the quantum form of equation (1) to the isomerization of cyclopropane, the reaction co-ordinate or dimension q_1 will be taken to be the diminution (from the equilibrium configuration) of the distance between a carbon and a non-adjacent hydrogen atom; there is, in this case, an extra factor of 12 in equation (1) corresponding to the number of distances of this type in the molecule. The same criterion for isomerization was used in the classical calculations in ref. 3; accordingly the vibrational parameters α_i and frequencies will be taken from Table 4 of that paper, with again $n = 13$ as the effective number of

¹ Falconer, Hunter, and Trotman-Dickenson, following paper.

² Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **217**, 563.

³ Slater, *Proc. Roy. Soc.*, 1953, *A*, **218**, 224.

⁴ Slater, "Theory of Unimolecular Reactions," Cornell Univ. Press, Ithaca, New York, and Methuen, London, 1959, Chapter X.

independent modes of vibration.* The quantum mean frequency ν may be treated as a constant, as it varies only from 4.12×10^{13} to 4.23×10^{13} over the temperature range that will be considered here.

The basic calculation for the present theory is of the sum (2) as a function of temperature. It is convenient to write

$$t = 1000/T \dots \dots \dots (3)$$

and to introduce in equation (2) the function (with $\alpha^2 = \sum \alpha_i^2$)

$$1/f(t) = \sum (\alpha_i^2/\alpha^2)(\nu_i/10^{13}) \coth (h\nu_i/2kT) \dots \dots \dots (4)$$

With the symmetry factor 12, the rate constant (1) is now written

$$k = 12\nu \exp \{-M \cdot f(t)\}, \quad M = 2q^2/(10^{13}h\alpha^2) \dots \dots \dots (5)$$

To match the range $T = 808-693^\circ$ of the experiments, the function (4) was calculated for the range

$$t = 1.24-1.44 \quad \text{with} \quad \Delta t = 0.02 \dots \dots \dots (6)$$

It will be sufficient here to represent these calculations by quoting the extreme and middle entries, namely:

$$f(1.24) = 0.233082, \quad f(1.34) = 0.244297, \quad f(1.44) = 0.254539 \dots \dots (7)$$

and also the approximate formula:

$$f(t) = A + Bt - \frac{1}{2}Ct^2 \dots \dots \dots (8)$$

where

$$A = 0.013179, \quad B = 0.237667, \quad C = 0.097300$$

This formula represents all the entries with an error under 5×10^{-6} .

The experimental results of Falconer *et al.* were close to the Arrhenius form

$$k_{\text{exp}} = 10^{15.3} \exp(-E_{\text{exp}}/RT); \quad E_{\text{exp}} = 65,084 \text{ cal. mole}^{-1} \dots \dots (9)$$

To gauge the discrepancy between this and the theoretical form, an estimate is required of the unknown parameter q or M in expression (5). This may be found by considering activation energy, although the choice of M is not unique, so that attention will be concentrated on relative changes of rate with temperature rather than on absolute values. The natural definition of E_a , the activation energy per mole, for a rate constant k is:

$$E_a/R = -\partial \ln k/\partial(1/T) = -1000\partial \ln k/\partial t \dots \dots \dots (10)$$

For the experimental form (9), $E_a = E_{\text{exp}}$. For the form (5), with the approximation (8) for $f(t)$, we have:

$$E_a/R = 1000M \cdot f'(t) \approx 1000M(B - Ct) \dots \dots \dots (11)$$

From the values of B and C above, this E_a is respectively 9% less and 9% greater at $t = 1.44$ and $t = 1.24$ than at the middle, $t = 1.34$, of the range (6).

To estimate M in expression (5), the temperature-dependent E_a of (11) is to be identified at some temperature with the experimental value in (9). If the middle value $t = 1.34$ is chosen in (11), then

$$M = (E_{\text{exp}}/R)/\{1000(B - 1.34C)\} = 305.31 \dots \dots \dots (12)$$

This gives for the exponent $M \cdot f(t)$ of the theoretical form (5), at $t = 1.44, 1.34, 1.24$, respectively,

$$77.713, \quad 74.586, \quad 71.162 \dots \dots \dots (13)$$

* Use should be made here of a new calculation of these parameters by A. P. Cox; but the revision is unlikely to affect the high-pressure rate constant, although it might affect lower-pressure rate predictions.

The corresponding values of E_{exp}/RT from (9) are

$$47.167, \quad 43.892, \quad 40.616 \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Comparing these numbers, we see that the increase in $\ln k$ between "temperatures" $t = 1.44$ and 1.24 is 6.551 in both (13) and (14), so that the relative increase in k is the same theoretically and experimentally over the total span of the temperature range. On the other hand, the difference between the first two numbers in (13) is 0.148 less than in (14). Thus the theoretical increase in $\log k = 0.4343 \ln k$ is 0.064 less than the experimental increase, in passing from the lowest to the "mean" temperature, that is, from $t = 1.44$ to 1.34 . This indicates that the theoretical plot of $\log k$ against $1/T$ is concave upwards, dipping below the linear experimental plot by an amount 0.064 at the middle of the range. The discussion of Falconer *et al.* indicates that this discrepancy considerably exceeds their experimental error.

If in identifying the activation energies an extreme value $t = 1.44$ or 1.24 were used in (12), a similar relative concavity would be found in the theoretical curve, although the values (13) of the theoretical exponent would change by $\pm 9\%$. The values (13) are in all these cases considerably larger than (14). Thus, as the remaining factor $12\nu = 5 \times 10^{14}$ in the theoretical rate constant (5) is similar to the experimental pre-exponential factor in (9), the absolute values of k on the present theory are much too small compared with the experimental values.

An Empirical Modification.—The limiting form of expression (2) as T tends to zero is

$$\sigma_0^2 = \frac{1}{4} h \sum \alpha_i^2 \nu_i \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

which is seen to be the zero-point mean square of the co-ordinate $q_1 = \sum \alpha_i Q_i$ with all oscillators Q_i in their ground states. It would seem plausible⁴ (although not in accord with the spirit of the original formulation of the present quantum model) to exclude all or much of the dispersion σ_0^2 from σ^2 in formulating the rate constant (1). The effect of such a modification may be tested by replacing σ^2 in (1) by $\sigma_1^2 = \sigma^2 - 0.756\sigma_0^2$. The rate constant (5) now becomes [with M defined as before in (5)]:

$$k = 12\nu \exp \{-M \cdot f_1(t)\} \text{ sec.}^{-1} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where $1/f_1(t)$ is the previously tabulated $1/f(t)$ decreased by a carefully chosen constant, which is in fact the source of the coefficient 0.756 in σ_1^2 above. With this choice, it is found that with an error generally under 6×10^{-6} , $f_1(t)$ can be represented as

$$f_1(t) = A' + B't \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where

$$A' = -0.095056, \quad B' = 0.440673$$

To this order of accuracy, the amended rate constant (16) is of an Arrhenius form, with activation energy given by $E_a/R = 1000MB'$ (cf. 11). Identifying this with the experimental value in (9) gives

$$M = 74.30 \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and for the rate constant (16)

$$k = 12\nu \exp \{-M(A' + B't)\} = 12\nu e^{7.065} \exp(-E_{\text{exp}}/RT) \quad . \quad . \quad (19)$$

The effective pre-exponential factor is now rather high, although the discrepancy is much less than in the previous calculation.

The effect of excluding zero-point contributions has also been briefly discussed in connection with the application of the present quantum theory to nitryl chloride,⁴ for which as for cyclopropane the simple classical theory gives a satisfactory picture. This

confirms the need for a fresh examination of the theoretical basis, since a correct theory must essentially be quantal; an exactly Arrhenius form of rate constant is not, however, to be expected.

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