The Attack of Methyl Radicals on Tetradeuterohydrazine

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GRAY and THYNNE[1] recently reported values of the velocity constants for hydrogen abstraction from hydrazine by methyl radicals:

$$CH_3 + N_2H_4 \rightarrow CH_4 + \cdot NHNH_2$$

They found that hydrogen abstraction was rapid over the temperature range studied (110 to 180°C), and that temperature-dependence of the velocity constant corresponded to an activation energy E_H of 5·0 ± 0·1 kcal. mole^{-1} and a pre-exponential factor A_H of 10^{11} cm.^{3} mole^{-1}sec.$^{-1}$ The size of A is normal for hydrogen abstraction by methyl radicals and corresponds to a value for the 'steric factor' P defined by the equation $k = PZ\,exp(-E/RT)$ of *ca.* 10^{-3}, if the effective collision-diameters for methyl and hydrazine are assumed to be *ca.* 3·5 and 5 Å respectively.

We have now studied the abstraction of deuterium from N_2D_4 over the same temperature range using azomethane as the methyl radical source. The results can be fitted by the Arrhenius equation: (errors quoted are standard deviations of a least-mean-squares treatment): $\log_{10}(k_{N_2D_4}/\text{cm.}^3\text{mole}^{-1}\text{sec.}^{-1}) = (10{\cdot}86 \pm 0{\cdot}17) - (6390 \pm 320)/2{\cdot}303\,RT$. Since previous experiments in which hydrogen attached to nitrogen has been replaced by deuterium have shown that the activation energy for abstraction is generally increased by 1 to 2 kcal. mole^{-1}, the activation energy of 6·4 kcal. mole^{-1} found here substantiates the rather low value found for hydrazine. By combining the results for N_2H_4 and N_2D_4 it is possible to assess quantitatively the primary isotope effect due to substitution of D for H. At 150°C, the quotient (k_H/k_D) is 7·0 ± 0·6. The errors in the Arrhenius parameters are larger: the difference in activation energies, $(E_D - E_H)$ is 1·4 ± 0·3 kcal. mole^{-1} and $\log(A_D/A_H) = \bar{1}{\cdot}14 \pm 0{\cdot}18$, corresponding to $(A_D/A_H) = 0{\cdot}72$.

The simplest interpretation of kinetic isotope effects is based on the assumption that on passing from the reactants to the transition state the

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[1] P. Gray and J. C. J. Thynne, *Trans. Faraday Soc.*, 1964, **60**, 1047.

zero-point energy associated with the stretching vibration of the bond being attacked is lost. It thus predicts that

$$(k_{\mathrm{H}}/k_{\mathrm{D}}) = exp\ (\Delta\overset{*}{E}_{\mathrm{H}} - \Delta\overset{*}{E}_{\mathrm{D}})/RT \qquad (1)$$

where $\Delta\overset{*}{E}_{\mathrm{H}}$ and $\Delta\overset{*}{E}_{\mathrm{D}}$ are the respective *decreases* in zero-point energy attending the passage from reactants to the transition state in the cases of H- and D-transfer. This relation is readily tested by observation.

This simple treatment also implies that $(A_{\mathrm{H}}/A_{\mathrm{D}}) = 1$ and that $(E_{\mathrm{D}} - E_{\mathrm{H}}) = (\Delta\overset{*}{E}_{\mathrm{H}} - \Delta\overset{*}{E}_{\mathrm{D}})$, although in gas-phase free-radical reactions it is usually impossible to determine separate values for A and E of sufficient accuracy to demonstrate statistically significant deviations.

From equation (1) it is possible to calculate the kinetic isotope effect. To the stretching vibration of an N–H bond in N_2H_4 has been assigned[2] a value 3325 cm.$^{-1}$ and the N–D stretching vibration, calculated using the formula $(\nu_{\mathrm{H}}/\nu_{\mathrm{D}} \simeq (M_{\mathrm{D}}/M_{\mathrm{H}})^{\frac{1}{2}}$, is *ca.* 2350 cm.$^{-1}$ This yields $(k_{\mathrm{H}}/k_{\mathrm{D}})_{\mathrm{calc}} = exp\ (1400/RT)$, which gives a value of 150°C, of $(k_{\mathrm{H}}/k_{\mathrm{D}})_{\mathrm{calc}} = 5{\cdot}29$. As seen above the experimental value for $(k_{\mathrm{H}}/k_{\mathrm{D}})$ is 7·0, which is significantly greater. In other experiments involving the abstraction of hydrogen and deuterium attached to carbon similar observations have been made. They have been explained in two different ways.

(a) Several workers[3,4] have proposed that the rates of these reactions are determined by an appreciable contribution from quantum-mechanical tunnelling. Such contributions may show themselves in two further ways: values for $(A_{\mathrm{D}}/A_{\mathrm{H}})$ may be found greater than 2, the upper limit in the absence of tunnelling and values for $(E_{\mathrm{D}} - E_{\mathrm{H}})$ greater than $\Delta\overset{*}{E}_{\mathrm{H}} - \Delta\overset{*}{E}_{\mathrm{D}} = 1{\cdot}4$ kcal. mole^{-1} the difference in zero-point energies. Our results do not reveal these effects.

(b) Equation (1) above assumes that the only vibration lost in the transition state is the stretching vibration of the N–H bond broken. Salomon[6] has recently explained high values of $k_{\mathrm{H}}/k_{\mathrm{D}}$ for methyl abstractions from C–H and C–D bonds without involving quantum-mechanical tunnelling, by assuming that the bending vibrations of the C–H bond are also lost in the transition state. A similar explanation is adequate here.

(*Received, July 12th,* 1965; *Com.* 436.)

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