Kinetics of the Decomposition of the Propionyl Radical

By J. A. KERR and A. C. LLOYD
(*Edward Davies Chemical Laboratory, Aberystwyth*)

KINETIC studies[1,2,3] have indicated[4] a value for the heat of formation of the acetyl radical of -4 ± 2 kcal.mole^{-1} and a more recent thermodynamic study[5] of the equilibrium between iodine and acetaldehyde has confirmed $\Delta H_f^0(\text{MeCO}) = 5{\cdot}2 \pm 0{\cdot}8$ kcal.mole^{-1}. No such data exists for the propionyl radical and we now report kinetic results on the decomposition of this radical. The radicals were generated by the selective photolysis (3660 Å) of azoethane in the presence of propionaldehyde. By analogy with the acetyl radical system,[1] the suggested mechanism is:

$$(C_2H_5N)_2 + h\nu = 2C_2H_5 + N_2 \tag{I}$$

$$C_2H_5 + C_2H_5{\cdot}CHO = C_2H_6 + C_2H_5{\cdot}CO \tag{1}$$

$$C_2H_5{\cdot}CO + M = C_2H_5 + CO + M \tag{2}$$

$$2C_2H_5 = C_4H_{10} \tag{3}$$

$$C_2H_5 + C_2H_5{\cdot}CO = C_2H_5{\cdot}CO{\cdot}C_2H_5 \tag{4}$$

$$2\,C_2H_5{\cdot}CO = (C_2H_5{\cdot}CO)_2 \tag{5}$$

$$2C_2H_5 = C_2H_6 + C_2H_4 \tag{6}$$

The rate constant (k_2) for the decomposition of the propionyl radical is given by the function:

$$k_2k_3^{\frac{1}{2}}/k_4 = R_{\text{CO}}R_{\text{Bu}^n}^{\frac{1}{2}}/R_{\text{EtCOEt}}$$

where R = rate of formation of product X. By analysing for the carbon monoxide, n-butane, and diethyl ketone the temperature coefficient of the above rate function has been measured between 30° and 110° and can be expressed by the Arrhenius equation $\log(k_2k_3^{\frac{1}{2}}/k_4)$ (mole$^{-\frac{1}{2}}$ c.c.$^{\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$) = $(1{\cdot}50 \pm 0{\cdot}11) - (8{,}210 \pm 170/2{\cdot}3\boldsymbol{R}T)$ for a constant total pressure of reactants of $\sim$ 70 torr.

The above experimental temperature coefficient can be identified with the decomposition reaction on the reasonable assumption that the radical combination reactions (3) and (4) involve zero activation energy, and hence $E_2 = 8{\cdot}2$ kcal.mole^{-1}. Preliminary experiments indicate that this activation energy has been measured in the pressure fall-off region, confirming the prediction of O'Neal and Benson,[6] and hence the limiting high-pressure value is probably considerably higher. In keeping with the results for the acetyl decomposition reaction[1] it would seem reasonable to assume $E_2^{\infty} \simeq 12$ kcal.mole^{-1}.

The enthalpy change for the reactions

$$C_2H_5{\cdot}CO \underset{(-2)}{\overset{(2)}{\rightleftharpoons}} C_2H_5 + CO$$

is related to the activation energies of the forward and reverse reactions by the equation

$$\begin{aligned}\Delta H_{2,-2} &= \Delta E_{2,-2} + n\boldsymbol{R}T\\ &= E_2^{\infty} - E_{-2}^{\infty} + n\boldsymbol{R}T\end{aligned}$$

There is no experimental value of E_{-2}^{∞} but it should be similar to that for the reaction of methyl radicals with carbon monoxide,[1] *i.e.*, about 5 kcal. mole^{-1}. It follows that $\Delta H_{2,-2} \simeq 8$ kcal.mole^{-1} from kinetic measurements.

An approximate thermochemical value of $\Delta H_{2,-2}$ can be derived from ΔH_f^0 (EtCO) on the assumption that $D(C_2H_5CO\text{–}H) \simeq D(CH_3CO\text{–}H) =$ 88 kcal.mole^{-1}. Taking[7] ΔH_f^0 $(C_2H_5CHO) = -45{\cdot}7$ kcal. leads to ΔH_f^0 (EtCO) $= -10$ kcal.mole^{-1}. A similar value can be calculated on the assumption that $D(C_2H_5{\cdot}CO\text{–}CH_3) \simeq D(CH_3{\cdot}CO\text{–}CH_3) = 82$ kcal.mole^{-1}, and taking[8] ΔH_f $(C_2H_5{\cdot}CO{\cdot}CH_3) = -58$ kcal.mole^{-1}. From ΔH_f $(C_2H_5{\cdot}CO) = -10$ kcal.mole^{-1} and other enthalpy data,[4,9] it can be shown that $\Delta H_{2,-2} \simeq 9$ kcal.mole^{-1} as a thermochemical estimate. The agreement between the kinetic and thermochemical estimates of $\Delta H_{2,-2}$ is satisfactory but confirmation and a discussion of the *A*-factor for the decomposition reaction must await a fuller investigation of the pressure effect.

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