the method involves the following sequence of reactions: acetone-glycerol → acetone-glycerol α'-benzyl ether → glycerol α-benzyl ether → α,β-diglyceride α'-benzyl ether → α,β-diglyceride.

The procedure has been applied for the synthesis of optically pure *d*-α,β-distearin and *d*-α,β-dipalmitin.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WESTERN RESERVE UNIVERSITY]

Kinetics of the Thermal Decomposition of Straight Chain Paraffins[1]

BY R. E. BURK, LEONA LASKOWSKI AND H. P. LANKELMA

Several conflicting theories have been proposed for the mechanism of the thermal decomposition of straight chain paraffins. F. O. Rice[2] assumes that free radicals are formed in the initial step of the reaction. These free radicals are then able to undergo two types of reaction

$$C_nH_{2n+2} + C_{n_a}H_{2n_a+1} = C_{n_c}H_{2n_c+2} + C_{n_d}H_{2n_d+1}$$

or a further decomposition to give another radical

$$C_nH_{2n+1} = C_{n_b}H_{2n_b} + C_{n_c}H_{2n_c+1}$$

The relative proportion of each type of reaction is thought to be dependent upon probabilities which involve both energetic and structural factors. Rice has estimated the proportions of the various products which are to be expected on the basis of free radicals. Some observations have supported,[3] others have denied, such a mechanism.[4,5]

One of us[6] has developed an alternate theory based on initial decomposition to an olefin and a paraffin rather than free radicals. By assuming that every carbon–carbon bond is equivalent (with the possible exception of the end C atoms) and that reaction occurs when a given amount of energy, namely, the energy of activation, is accumulated in a single carbon–carbon bond, this theory is expressed by the following equation for the rate of decomposition (exclusive of dehydrogenation) of a straight chain paraffin

$$-\mathrm{d}N/\mathrm{d}t = N(n - 1)ve^{-E/RT} = Nk$$

where N is the total number of moles of reactant, n is the number of carbon atoms in the decomposing hydrocarbon, v is the vibration frequency of the carbon atoms composing a bond and is equal to about 3.45×10^{13}/sec., E is the energy of activation, and k is the reaction velocity constant. If the assumptions made to obtain this rate equation are tenable, the energy of activation, E, should be a constant regardless of the number of carbon atoms in the decomposing hydrocarbons.

When this equation was first proposed, data adequate for testing it were not available. Since that time, however, numerous investigations[3,7–16] have supplied test material resulting in the energies of activation shown in the accompanying graph. These values of the energies of activation were calculated from the experimentally determined reaction velocity constants using the Burk[6] equation for the rate of decomposition of a straight chain paraffin from which

$$E = 2.303RT[\log k - \log v\,(n - 1)]$$

All the values calculated have been plotted against the temperatures at which they were measured, using the same symbol for each value of E pertaining to a specified hydrocarbon. The reference is given alongside each symbol. No trend is evident for a functional relationship between the energy of activation and the particular hydrocarbon decomposing.

These values of the energy of activation vary from 59,000 to 65,000 g. calories per g. molecule. An average value of E cannot be obtained by the usual method of taking an arithmetic mean since the experiments are not equivalent. An error in temperature causes a proportional change in the energy of activation and an error in measuring the per cent. conversion occurs logarithmically. It seems more probable, however, that each experi-

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menter was consistent in the type of experimental error so that the energies of activation of each set of workers may be averaged, giving us these values in calories

Pease and co-workers	64,100
Dintses and co-workers	62,900
Marek and co-workers	63,440
Frey and Hepp	62,750
Marschner	62,510
Steacie and Puddington	62,880

With the exception of the Pease experiments these values agree very well, all lying in the range of 63,000 ± 500 calories. Pease's work should be discounted somewhat because his conversions were in general high, and he obtained the lowest energies of activation in the case of the lowest conversions.

The constancy of the energy of activation for the thermal decomposition of straight chain hydrocarbons calculated from experimentally determined velocity constants using the equation derived from the Burk mechanism, corroborates the assumptions of that mechanism.

The kinetics of the free radical mechanism for the decomposition of *n*-paraffin hydrocarbons proposed by Rice have been considered. This theory proposes that reaction begins (1) with the decomposition of the hydrocarbon to form two free radicals. The chain is carried (2) by radicals reacting with molecules to give a new molecule and a radical, and the reaction is ended (3) by the collision of two radicals.

To simplify the kinetics of the mechanism we have assumed that each radical formed may be considered an "average" free radical, R, so that

$$M_1 \xrightarrow{k_1} 2R \tag{1}$$

$$M_1 + R \xrightarrow{k_2} M_2 + R \tag{2}$$

$$2R \xrightarrow{k_3} R - R \tag{3}$$

The concentration of radical at any time can be found by solving the rate equation for formation of R.

$$\mathrm{d}R/\mathrm{d}t = k_1M_1 - k_3R^2 = 0 \tag{4}$$

so that

$$R = \sqrt{\frac{k_1M_1}{k_3}}$$

The rate of decomposition of hydrocarbon is then

$$-\mathrm{d}M_1/\mathrm{d}t = k_1M_1 + k_2M_1R = k_1M_1 + k_2M_1\sqrt{\frac{k_1}{k_3}M_1} \tag{5}$$

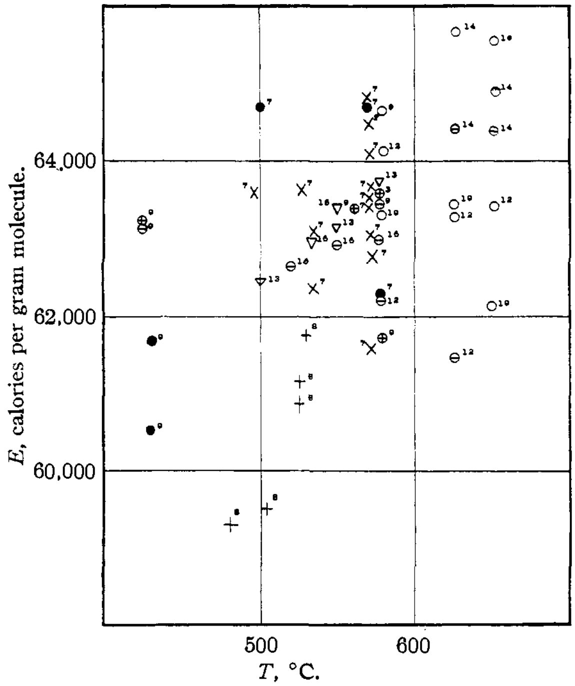

Fig. 1.—Experimental energies of activation of thermal decomposition of *n*-paraffin hydrocarbons: O, propane; ⊖, butane; ⊕, pentane; ●, hexane; ▽, heptane; ×, octane; +, dodecane.

The rate constants for the steps in the reaction can be evaluated. The reaction rate constant for the primary decomposition into radicals k_1, is obtained from the equation for the thermal decomposition of straight chain paraffins

$$k_1 = (n - 1)ve^{-E_1/RT}$$

The remaining steps in the free radical mechanism are bimolecular reactions carried on by collisions. Their reaction velocity constants may be evaluated as follows

$$k_2 = c_1\sqrt{T}(\sigma_{\mathrm{M}} + \sigma_{\mathrm{R}})^2e^{-E_2/RT} \tag{6}$$

$$k_3 = c_2\sqrt{T}\sigma_{\mathrm{R}}^2e^{-E_3/RT} \tag{7}$$

where c_1 and c_2 are constants which include steric factors. T is the absolute temperature, σ_{M} is the collision radius of the decomposing hydrocarbon, and σ_{R} is the collision radius of the average radical formed.

Rice[2] proposes these values for the energies of activation: E_1 = 80,000 cal.; E_2 = 15,000 cal.; E_3 = 8000 cal. Substituting the values for k in equation (5)

$$\frac{-\mathrm{d}M}{\mathrm{d}t} = M(n - 1)ve^{-E_1/RT} +$$

$$CM^{3/2}\frac{(\sigma_{\mathrm{M}} + \sigma_{\mathrm{R}})^2}{\sigma_{\mathrm{R}}}e^{-\frac{(E_1 + 2E_2 - E_3)}{2RT}}\left[(n - 1)v\sqrt{T}\right]^{1/2} \tag{8}$$

The collision radii of the straight chain paraffins have been calculated from collision areas reported by Melaven and Mack with the results given in Table I.

Table I

Experimental Collision Radii of Hydrocarbons

Hydrocarbon	Collision area, sq. Å.	Radius	a
Ethane	10.63	1.84	0.23
Propane	13.53	2.07	.21
Butane	16.11	2.26	.21
Heptane	26.7	2.96	.25
Octane	34.9	3.33	.26
Nonane	42.5	3.68	

The column marked a was calculated by subtracting the ethane length from each of the higher hydrocarbons and dividing the residue by $n - 2$ where n is the number of carbon atoms in the hydrocarbon. This value appears to be fairly constant although it may be a function of the number of carbon atoms in the hydrocarbon chain. Assuming that a has an average constant value, we see that the collision radius of a hydrocarbon, σ_M, is $a(n - 2) + 1.84$ Å. Substituting this value of σ_M in equation (8) and at the same time taking $[(v/\sigma_R)^{1/2}]$ into the constant C, we have

$$\frac{-\mathrm{d}M}{\mathrm{d}t} = Mv(n - 1)e^{-E_1/RT} + CM^{3/2}T^{1/4}e^{-(E_1 + 2E_2 - E_3)/2RT}(n - 1)^{1/2}[a(n - 2) + 1.84 + \sigma_R] \quad (9)$$

This simplified chain mechanism is faster than the experimental rate. The dominant rate factor in the free radical mechanism is the chain rather than the initial step, so that the rate of decomposition for the simplified chain is proportional to $(n - 1)^{1/2}(n - 2)^2$ where n is the number of carbon atoms in the decomposing hydrocarbon. The rate determining factor in the molecular mechanism which has been shown to fit experiment is proportional to $(n - 1)$.

If relative rates of reactions are considered, octane should decompose proportionally to $(8 - 2)^2(8 - 1)^{1/2}$ and propane, $(3 - 2)(3 - 1)^{1/2}$. According to the free radical mechanism, octane should decompose 68 times as fast as propane, but it actually decomposes only 3.5 times as fast. Thus octane by a simplified free radical mechanism should decompose 19.5 times as fast as it does.

This argument could be circumvented by assuming an increasing steric factor for reaction (2) as the series is ascended, which just compensates the accelerating effect of increase in target area. But this could scarcely be regarded as a probable assumption. The authors appreciate the strength of evidence supporting chain mechanisms for hydrocarbon decompositions and continue to view the whole question open-mindedly.

Summary

The constancy of the activation energy for the thermal decomposition of a straight chain paraffin calculated from experimentally determined velocity constants using the equation

$$-\mathrm{d}M/\mathrm{d}t = M(n - 1)ve^{-E/RT} = Mk$$

derived from the Burk mechanism which assumes equally probable scission of C–C bonds to form an olefin and a new hydrocarbon, corroborates the assumptions of that mechanism.

The rate of decomposition for a simplified chain mechanism has been shown to be proportional to a power of n at least as great as $(n - 2)^2(n - 1)^{1/2}$ where n is the number of carbon atoms in the decomposing hydrocarbon. Such a proportionality predicts a rate of decomposition many times more rapid than experiment.

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