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APPLICATION OF COMBINED PYROLYSIS–THIN-LAYER CHROMATOGRAPHY TO THE STUDY OF CHEMICAL KINETICS

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SUMMARY

The theory of the thermal decomposition of a pure liquid is discussed, and limitations on the determination of true kinetic constants are specified. True kinetic constants cannot be obtained from a complex first-order reaction without studying the component reactions separately. Methods for studying component reactions by use of programmed-temperature pyrolysis combined with TLC are presented. The methods are used to determine activation energies for the thermal decomposition of some monosaccharides.

INTRODUCTION

Most organic decomposition reactions occur at appreciable rates only after the compound has melted. When the reaction proceeds homogeneously without dilution of the reactant by the reaction products, *i.e.*, products are gases and/or immiscible liquids or solids, the rate of the reaction should be proportional to the number of activated complexes present at any instant. The number of activated complexes is simply proportional to the amount of reactant present; therefore, the rate equation should take the form*

$$- da/d\tau = ka \tag{1}$$

The importance of the foregoing is that, if the decomposition of a pure liquid conforms to the model, the reaction of necessity is first order in weight of reactant. If the reaction order is not 1, the reaction is complex.

If a reaction is complex, no method that measures the overall rate of disappearance of reactant can give true kinetic constants; the best that can be obtained is a "procedural activation energy" and associated preexponential. These numbers may be useful in designing process equipment, but they are not directly related to the basic chemistry of the system.

The fact that decrease in reactant obeys a first-order expression is necessary but not sufficient to indicate a simple reaction. The reaction can be composed of

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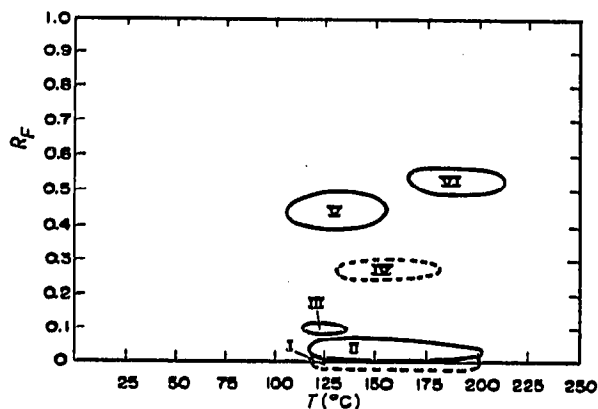* A glossary of terms appears at the end of this paper.

Fig. 1. Tracing of pyrolysis–TLC plate. Sample, 1.0 mg levulose wet with H_3PO_4; heating rate, 11 °C/min; carrier gas flow, 50 ml/min N_2; chromatographic development with 1,2-dichloroethane; visualization with UV, I_2 vapor, and aniline phthalate. (I) probably formic acid, $R_F = 0$; (II) levulinic acid, $R_F \sim 0.03$ (this system is poor for levulinic acid); (III) hydroxymethylfurfural, red with aniline phthalate, $R_F = 0.094$; (IV) unidentified; (V) furfural, red with aniline phthalate, $R_F = 0.44$; (VI) 3-pentenoic-γ-anhydride (pyrolysis product of levulinic acid), $R_F = 0.55$.

several first-order or pseudo first-order component reactions. If such is the case, each of the component reactions should be studied separately.

Under favorable conditions one of the simplest ways to obtain rate information about specific thermal decomposition products appears to be by application of combined pyrolysis and thin-layer chromatography[1]. This technique involves heating a sample under a flowing carrier gas stream at a programmed rate (or isothermally) while impinging the carrier gas stream containing the decomposition products onto the surface of an activated TLC plate. The plate is transported across the orifice of the pyrolysis system as a function of sample temperature (or as a function of time for an isothermal system). Therefore, any position along the zone of application of the plate corresponds to a specific sample temperature. The plate can then be developed by usual chromatographic techniques to separate the individual products of the reaction. The final plate yields two types of data: R_F data in the direction of development, and temperature (or time) data along the zone of application. An example of such a pyrolysis–TLC plate is shown in Fig. 1. Each product zone can then be photometered to give relative quantities as a function of temperature or time. In this paper we will consider methods for extracting kinetic data from programmed-temperature runs on reactants that decompose by first-order kinetics.

We first consider the one-reaction system represented by the equations

$$A \to \nu X \tag{2}$$

and

$$- \, da/d\tau = ka = aZe^{-E/RT} \tag{3}$$

Under programmed-temperature conditions T is a function of time: $T = T(\tau)$. If $a = a_0$ at $\tau = 0$ and $a = a(t)$ at $\tau = t$, then, from eqn. 3,

$$- \int_{a_0}^{a(t)} d \ln a = - \ln \frac{a(t)}{a_0} = Z \int_0^t e^{-E/RT} \, d\tau, \tag{4}$$

whence

$$a(t) = a_0 \, e^{-Z\int_0^t e^{-E/RT}\,d\tau} \tag{5}$$

The rate of formation of X is

$$dx/d\tau = -v\,da/d\tau = vka = vaZe^{-E/RT} \tag{6}$$

If the rate of formation of X is determined with an instrument having a linear response and a sensitivity $1/\alpha$, then

$$dx/d\tau = \alpha b \tag{7}$$

From eqns. 6 and 7,

$$\ln b = \ln \frac{vZ}{\alpha} + \ln a - \frac{E}{RT} \tag{8}$$

and

$$\frac{d\ln b}{d(1/T)} = -\frac{E}{R} - \frac{T^2}{a}\frac{da}{dT} \tag{9}$$

If we now restrict ourselves to the usual condition of a linear programming rate then $T = T_0 + B\tau$, $dT = Bd\tau$, and eqn. 9 becomes

$$\frac{d\ln b}{d(1/T)} = -\frac{E}{R} - \frac{T^2}{B}\frac{1}{a}\frac{da}{d\tau}$$

$$= -\frac{E}{R} + \frac{kT^2}{B} \tag{10}$$

This implies that, when

$$k \ll BE/RT^2 \tag{11}$$

the value of $-E/R$ is given by the slope of a plot of $\ln b$ vs. $1/T$. This condition is, of course, satisfied only during the initial stages of the reaction, when T and k are low.

At the maximum in the plot of $\ln b$ vs. $1/T$

$$kT_m^2/B = E/R \tag{12}$$

whence

$$Z = \frac{B\,E\,e^{E/RT_m}}{RT_m^2} \tag{13}$$

Thus the observed value of T_m can be used with an initial estimate of E to obtain an estimate of Z. Then k can be calculated as a function of T, and the original estimate of E can be refined by means of eqn. 10. This suggests that an iteration on eqns. 10 and 13 might produce useful estimates of E and Z even when the condition expressed by eqn. 11 is not well satisfied.

We can now generalize these results to the case of simultaneous first-order

reactions, represented by

$$A \rightarrow \nu_i X_i, \; i = 1, 2, \ldots . N \tag{2a}$$

and

$$- \, da/d\tau = ka \tag{3a}$$

where $k = \Sigma k_i$ with $k_i = Z_i \, e^{-E_i/RT}$. Proceeding as before, with

$$dx_i/d\tau = - \, \nu_i \, k_i \, da/kd\tau = \nu_i \, k_i \, a = \nu_i \, a \, Z_i \, e^{- \, E_i/RT} \tag{6a}$$

and

$$dx_i/d\tau = \alpha_i \, b_i \tag{7a}$$

we obtain

$$\ln b_i = \ln \frac{\nu_i Z_i}{\alpha_i} + \ln a - \frac{E_i}{RT} \tag{8a}$$

and

$$\frac{d \ln b_i}{d(1/T)} = - \frac{E_i}{R} + \frac{kT^2}{B} \tag{10a}$$

The analogue of eqn. 11 is now

$$k \ll BE_i/RT^2 \tag{11a}$$

In this case, then, activation energies can be obtained directly from the slopes of the $\ln b_i$ *vs.* $1/T$ plots only for those products that produce a useful response while the *total* rate constant remains small compared to BE_i/RT^2.

If this condition is satisfied well enough to obtain reasonable initial estimates of the E_i for all the products, then the iteration scheme may still be used with eqn. 13 replaced by

$$BE_i/RT_{m_i}^2 = \Sigma_j Z_j \, e^{- \, E_j/RT_{m_i}}, \quad i, j = 1, 2, \ldots . N \tag{13a}$$

If useful estimates of the Z_i can be obtained from these N simultaneous linear equations, k can be calculated as a function of T, and the initial estimates of the E_i can be refined by means of eqn. 10a.

The discussion to this point applies to experimental conditions such that the only data collected are based on rates of product formation. Note, however, that when the rate constant for the overall reaction is known or can be determined, the correct activation energy for any component reaction can be calculated from the rate data for a specific product by use of eqn. 10a.

An estimation of the degree to which the condition specified by eqn. 11a is met by any or all of the products of a complex reaction can be obtained by reference to the pyrolysis–TLC plate. The product that appears at the lowest temperature is most likely to meet the condition. The iteration should not be attempted unless all the products appear at approximately the same temperature.

To this point extraction of kinetic data from single rate curves has been considered, but KISSINGER[2] and DANEŠ AND PONEC[3] presented a method for the determination of kinetic constants from multiple decompositions at different heating

rates. Using the KISSINGER method, results are interpreted according to the expression

$$\ln B/T_m{}^2 = E/RT_m + c \tag{14}$$

which can be extended to the component reactions of an overall first-order complex reaction. However, as discussed above, if the overall reaction is not first order, none of the present methods can yield true kinetic constants. Therefore, reaction order should be investigated before proceeding with any kinetics analysis.

KISSINGER also presented a method for the estimation of reaction order from the symmetry of a differential thermal analysis (DTA) curve[2]. This method is unlikely to provide accurate results when applied to single-product rate curves, but it can be used for the detection of complexity in the various reactions. If the apparent order as estimated by KISSINGER's method is found to vary appreciably with heating rate, the reaction is complex.

RESULTS AND DISCUSSION

We have pointed out that unless a condensed-phase decomposition shows a reaction order approximating one the reaction is complex and cannot yield valid kinetic constants directly. However, a reaction may obey a first-order expression and still be complex, being the summation of multiple first-order component reactions. In the latter case, kinetic constants obtained from a study of the disappearance of reactant will be "procedural".

We have presented the basic equation (eqn. 10a) that allows kinetic constants for component first-order reactions to be calculated from single-product rate data. We have also noted that a method designed to obtain kinetic constants from multiple DTA runs at different heating rates[2,3] can be used to analyze pyrolysis–TLC data.

In order to test methods for extracting kinetic constants from rate information, it is obvious that some well known reaction should be run, and the results should be checked with the literature values. However, it has been impossible to find definitive results on suitable condensed-phase systems reported in the literature that can be used for comparative purposes. A few scattered data that could be used to check the accuracy and utility of the methods we wished to study were found in the literature on carbohydrates. Distinct advantages of studying the pyrolysis of sugars are that differences between isomeric sugars, e.g., between pyranose and furanose forms, and differences between parallel component reactions can be studied, allowing comparisons to be made where absolute values are missing. Simultaneous measurement of the rates of the component reactions would allow eqn. 10a to be tested.

The only monosaccharides that could be obtained at our laboratory in a good state of purity and well characterized were arabinose (a pyranose), ribose (as the furanose), and levulose (pyranose, hexose). Polysaccharides were eliminated from consideration because of a lack of suitable literature data for comparison; activation energies from 14 to 42 kcal/mole have been published for the decomposition of cellulose, for example.

Each sugar was first studied according to its rate of production of furfural, using silica gel TLC plates developed with 1,2-dichloroethane. The furfural was detected by spraying the plates with aniline phthalate reagent, and the colored band was photometered.

TABLE I

APPARENT REACTION ORDER ACCORDING TO CURVE SYMMETRY AS A FUNCTION OF HEATING RATE

Heating rate	Reaction order (n)			
	Ribose	Ara- binose	Levulose	RDX
Low	2.2	0.7	1	1
Intermediate	2.2	—	1	0.7
High	2.1	0.7	1	0.6

Since the first requirement for making a kinetics analysis was the establishment of the degree of complexity of the reactions, apparent reaction order as a function of heating rate was estimated for each major component reaction by KISSINGER's method. Results for the furfural reaction are presented in Table I. While apparent orders for the component reactions are not one in every case, their constancy at different heating rates is taken to imply that the true order of each and the overall order are one. Many references state that the overall rate of disappearance of such monosaccharides follows a first-order law. Values obtained from a similar analysis of the decomposition of the explosive RDX (hexahydro-1,3,5-trinitro-s-triazine) according to the rate of appearance of formaldehyde are included for comparative purposes. The decomposition of RDX is known to be complex, involving both auto-catalysis and inhibition, and the apparent order is not constant with heating rate.

After establishing the fact that the decompositions could be analyzed, the rate of furfural production from each of the sugars was analyzed by use of the KISSINGER method. As an example of the method, the data for the decomposition of ribose at different heating rates between 4°/min and 21°/min are shown in Table II. Results obtained from the three sugars with regard to the furfural reaction are presented in Table III. Note that the activation energy for the pentose in the pyranose form (arabinose) is much higher than for the pentose in the furanose form (ribose). The activation energy for opening a pyranose ring has been measured[4] as 16.5 kcal/mole, representing a sizable portion of the overall activation energy for the production of

TABLE II

DATA FROM RIBOSE DECOMPOSITIONS AT VARIOUS HEATING RATES

$1/T_m \times 10^3$	$\log B/T_m^2$
1.918	— 5.8904
2.025	— 6.5631
2.059	— 6.5489
2.070	— 6.5440
1.908	— 5.8946
1.908	— 5.8950
2.018	— 6.1269
2.014	— 6.1286

Slope = — 4094.59
Intercept = 1.9494
Activation energy, E = 18.75 kcal/mole

TABLE III

ACTIVATION ENERGIES OF SUGARS BASED ON FURFURAL REACTION, DETERMINED BY MULTIPLE HEATING RATE METHOD ACCORDING TO eqn. 14

Sugar	Form	E (kcal/mole)
Arabinose	pyranose	26.9
Ribose	furanose	18.8
Levulose	pyranose	26.7

furfural. It is stated that the pyranose ring is considerably more stable than the furanose ring[5]; therefore, the activation energy for the production of furfural from a pyranose should be larger than that for a furanose. The absolute values for the pentoses can be compared with a literature value. An extensive set of rate constants for the production of furfural from xylose (as a pyranose) was published by SCHOENE-MANN[6]. Reducing the data to obtain an activation energy gave a value of 28.8 kcal/mole. Arabinose and xylose should be nearly identical, differing only by a small energy of mutarotation. Under the circumstances it would appear that agreement is quite good.

Published values for activation energies for hexose decompositions ranging from zero to approximately 32 kcal/mole can be found, making a study of a hexose almost useless for the determination of accuracy. However, the mechanism of the complex hexose decomposition has been studied in some detail[7], making comparisons possible.

In order to make comparisons and to obtain an indication of the limitations imposed on the use of single rate curves for individual products, a particularly smooth photometer curve for levulose (Fig. 2) was chosen for more careful study. The curve was integrated graphically by use of a planimeter every 0.1 in. throughout its span, and rates, heights, areas, and temperatures were tabulated for each of the 51 points used. The results obtained at different extents of reaction by use of the different methods for analyzing a single curve are compared in Table IV. In column I it is
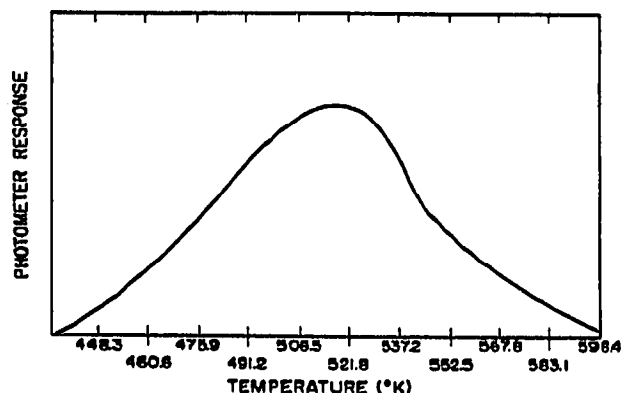

Fig. 2. Photometer curve for production of furfural from levulose. 2.098 mg sample; pyrolysis at 4 °C/min; N_2 carrier gas flowing at 35 ml/min; silica gel plate developed with 1,2-dichloroethane; visualization by spraying with aniline phthalate; photometered with Nester-Faust Uniscan 900 using blue-green filter.

TABLE IV

COMPARISON OF ACTIVATION ENERGIES CALCULATED FOR THE COMPONENT REACTION FROM THE RATE OF PRODUCTION OF FURFURAL FROM LEVULOSE (Fig. 2)

(I) $E_i = -R(d \ln b_i/d(1/T)$; (II) Assumes $k = k_i$, iterating between eqns. 10 and 13; (III) From $\ln b_i = -E_i/RT + c$; (IV) Multiple regression analysis of $dx/dt = a\, Z_i \mathrm{e}^{-E_i/RT}$, assuming $a = a_0 - x/v$; (V) From eqn. 10a, assuming $k_{\mathrm{total}} = k_{\mathrm{furfural}} + k_{\mathrm{levulinic\ acid}}$.

% Decompo-sition	E_1 (kcal/mole)				
	I	II	III	IV	V
5	19.5	21.5	28.5	51.3	23.9
15	15.5	19.0	27.2	34.5	23.8
25	10.0	16.6	23.7	31.4	26.6

assumed that the correction kT^2/B is negligible, a procedure that leads to considerable inaccuracy as the extent of reaction increases. This method gives an activation energy that decreases monotonically with extent of decomposition; the E would appear to become zero at T_m. In column II eqn. 10a is used with the assumption that the total k is approximately the same as the k for the component reaction. Column III shows results from a least-squares fit of $\ln b_i = -E_i/RT + c$ up to the indicated % decomposition. As predicted by eqn. 10a, E decreases as the extent of decomposition increases, but useful results can be obtained. Column IV shows the results from a multiple regression analysis of $\ln dx/d\tau = \ln Z_i + n \ln a - E_i/RT$, assuming that $a = a_0 - x/v$. Column V shows the results from a direct application of eqn. 10a, obtaining the total rate constant from the summation of the constants for the furfural and levulinic acid reactions. The E shown is the result of 3–5 iterations. Drift in the values appears to have been largely eliminated, and reasonably good agreement with the value presented in Table III is obtained.

Hexoses, especially levulose, reportedly produce hydroxymethylfurfural as a primary product of decomposition[7]; however, the compound is quite unstable. Hydroxymethylfurfural is reported to give a quantitative yield of levulinic acid under proper conditions, but furfural can be detected on the TLC plates (Fig. 1). Formaldehyde, the other product expected in the reaction giving furfural, has been detected by pyrolysis–TLC. However, the preferred production of levulinic acid suggests that it should be the lower energy process. Using the proposed method, it is possible to compare the two reactions. Results were as follows: levulose to furfural, $E = 26.7$ kcal/mole; levulinic acid, $E = 18.7$ kcal/mole. The results are certainly in the correct order, and they appear to be of the correct magnitude.

We believe that agreement between our results and literature values, especially that derived from the excellent data of SCHOENEMANN[6], the internally consistent results obtained by the different methods, and comparisons between pyranose and furanose forms and parallel reactions show that it should be possible to obtain reasonably accurate kinetic constants by use of the pyrolysis–TLC method. The method provides a simple, unique way to determine the kinetic constants of the component reactions of a complex process, within the limitations discussed.

Recognizing the difficulty involved in making a complete analysis of the rates of appearance of all of the products of a complex reaction and the limitations inherent

in obtaining constants from a single-product rate curve, shown by eqn. 10a, the best approach to single-curve kinetics analysis should be by way of a combination of techniques. For example, a combination of programmed-temperature thermogravimetry with temperature-based TLC measurement of products should make it possible simultaneously to determine overall reaction constants and constants for the component reactions for which measurements can be made. Kinetic constants for a component reaction could then be obtained directly from eqn. 10a, or from a multiple regression analysis of the equation

$$\ln b = \ln Z_i/\alpha + n \ln a - E_i/RT \tag{15}$$

from which an independent determination of reaction order could be obtained.

GLOSSARY

A = reactant
a = amount of A present at any instant
α = proportionality constant between reaction rate and instrument response
B = heating rate (°C/sec)
b = photometer (recorder) response (mm)
c = a constant
DTA = differential thermal analysis
E = activation energy
E_i = activation energy of a component reaction
k = rate constant
n = reaction order
v = stoichiometric coefficient
R = gas constant
R_F = relative migration rate
RDX = hexahydro-1,3,5-trinitro-s-triazine
T = temperature
T_m = temperature at curve maximum
t,τ = time
X = product
x = amount of product
Z = Arrhenius preexponential (sec^{-1})

ACKNOWLEDGEMENT

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SECTION V

COMBINATION OF PAPER OR THIN-LAYER CHROMATOGRAPHY WITH OTHER CHROMATOGRAPHIC PRINCIPLES