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A SIMPLE PRINCIPLE OF REACTION CALORIMETRY

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ABSTRACT

A new measuring principle for following a rate of heat evolution in exothermic reactions under isothermal conditions has been proposed and experimentally tested. The reaction is carried out in an insulated vessel equipped with a cooling coil. The reaction heat is removed by stepwise addition of a coolant into the cooling coil. Using the oxidation of ethanol by hydrogen peroxide catalyzed by ferric ions as a model reaction, practically the same precision in estimation of rate data has been achieved with this thermokinetic method as with the chemical analysis of reaction mixture.

INTRODUCTION

In recent years a steadily growing interest in reaction calorimetry is clearly noticeable[1]. There are many reasons for revamping interest in this old method, as e.g.

- need for reliable data for scalling-up laboratory reactors into production size e.g. in pharmaceutical industry,
- estimation of kinetic parameters in processes for which direct measurement of conversion by method of chemical analysis is impractical or even impossible,
- full evaluation of all possible reaction thermal hazards,
- reduction of energy consumption and cost,
- process optimization and development, etc.

One of the latest developments in this field is so called "preparative" reaction calorimetry[2], or a "mini-pilot" reaction calorimetry[3] permitting to carry out chemical reactions in relatively large "preparative" volumes,e.g. in 500 to 2.500 ml range, in practically ordinary reaction flask under widely varying conditions, and at the same time to measure the heat produced with sufficient accuracy. Such preparative reaction calorimetry are almost invariable the heat-flow type.

In our present work we studie a new measuring principle exploitable for the above stated purpose.

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PRINCIPLE OF THE METHOD

The reaction is carried out in an insulated reactor equipped with a cooling coil. The reaction heat is compensated by stepwise feeding of a coolant into the cooling coil. The method is based on an assumption, that the heat transfer area is in sufficient excess, consequently, the cooling agent is leaving the system with temperature T_e which equals the reaction temperature T_r, i.e.

$$T_r = T_e \qquad (1)$$

Then, if the inlet temperature of a coolant is constant, the manipulated flow rate is a measure of the heat production rate and the total amount of cooling medium which passed the system gives information about heat of reaction.

For isothermal reaction control an on-off regulator was used. Coolant was fed into the coil only if the T_r went beyond the noise bandwith of preset value. Electromagnetic valve then opened a constant flow rate of coolant to add a volume ΔV_c, which has to be smaller than the total inner volume of cooling coil. From a predetermined values of flow rate of coolant and times of valve openings the instantaneous flow rate (differential data), or the time dependence of total amounts of coolant (integral data) may be obtained. For the evaluation of the total heat balance it is necessary to estimate also the secondary heat effects,i.e. the heat loss to the surroundings and a possible heat input from an impeller. The overall reaction heat output may be calculated from the following relation:

$$Q = \sum_{n=1}^{n=n} \Delta V_c \rho_c c_{pc} \left(T_r - T_{ci} \right) + Q_{sec} \qquad (2)$$

where Q_{sec} is the sum of all secondary heat effects, T_{ci} is the inlet temperature of a coolant with specific heat c_{pc}, n is the number od stepwise additions.

MEASURING METHODS

Apparatus. Reaction calorimeter has been constructed from a conventional Dewar flask (1,Fig.1), 0.57 l, inside of which a cooling coil was placed. The coil is made from PTFE tubing 2.5 mm i.d. and 4.99 m of total lenght, supported by a glass rack. Reactor was also equipped with impeller, calibration heating elements and thermocouples.

The coolant (water) was kept at constant temperature T_{ci} in a reservoir 2 above the calorimeter and flows to the coil by gravity. The temperatures T_r,T_e, and T_{ci} were measured by thermocouples and were recorded on linear recorder or they were fed into desk-top computer. The electromagnetic valve 3 was operated by hand according to the recorder readings or automatically by computer. The deatils of computer algorithm and programs will be published elsewhere.

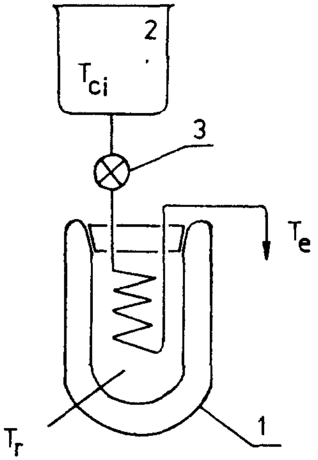

Fig.1 Scheme of reaction calorimeter

Model reaction. The oxidation of ethanol with hydrogen peroxide catalyzed by ferric ions has been used as a model reaction. By varying the starting concentrations of reactants and that of the catalyst, it is possible to adjust the heat output as well as the rate of reaction accordingly. We used the following range of cencentrations (in $mol.l^{-1}$): H_2O_2 0.3-0.6, ethanol 0.2-0.5, and $Fe(NO_3)_3$ $3.0-3.5x10^{-3}$. Heat of reaction was determined experimentally in separate experiments, the value found was -277 $kJ.mol^{-1}_{H_2O_2}$. Reaction has a first-order time dependence in both peroxide and catalyst and it is a zero-order in ethanol. For comparison the course of reaction was monitored analytically by titration of withdrawn samples with permanganate.

RESULTS AND DISCUSSION

It was proved that by this measuring principle an exothermic reaction can be carried out under isothermal conditions and sufficiently precise thermokinetic data are obtainable. Stepwise addition of coolant can satisfactorily control the reaction temperature. The volumes of additions has to get smaller in the course of reaction because the ΔV_c which is necessary for keeping the rate of heat evolution under control at the start of reaction, is excessive in the later stages and brings about a large undercooling or reaction mixture.

On Fig. 2 the actual course of reaction temperature together with amounts of each ΔV_c are illustrated for the simplest possible experimental setup, i.e. when the regulatory valve was operated by hand. Even from this data the kinetic parameters may be at least approximately estimated. If the desk-top computer is used for the control of experiment, the course of reaction temperature is much more smoother and, consequently, the kinetic data can be determined with substantially higher precision. The following experimentally determined rate constants for model reaction at 58 °C illustrate the precision attainable with different methods:

- reaction calorimeter operated by hand: $k = (1.61 \pm 0.48) x 10^{-3} s^{-1}$
- react.calorim. under computer control: $k = (1.63 \pm 0.13) x 10^{-3} s^{-1}$
- chemical analysis: $k = (1.65 \pm 0.69) x 10^{-3} s^{-1}$

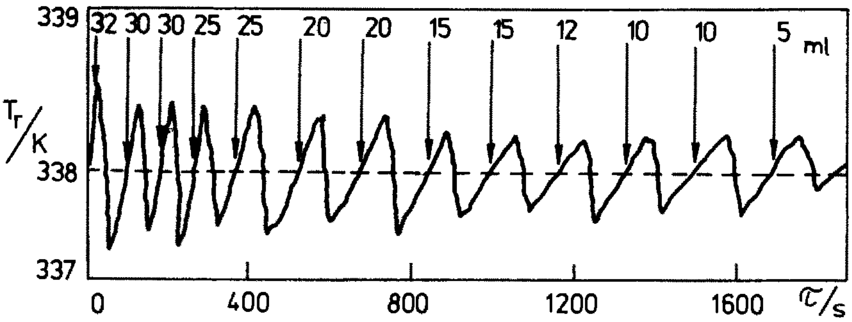

Fig. 2 Course of reaction temperature and the amount of coolant additions under hend control

These results indicate that valuable information can be obtained with simple design of reaction calorimeter and that the data obtained are comparable with results from much more sophisticated instruments. A hand control of measurements is acceptable for preliminary estimation but employment of laboratory computer is advisable for serious work.

REFERENCES

1. J. Horák, J. Šilhánek, Chem.Prům., in press
2. W. Regenass, Thermochim. Acta 20 (1977) 65
3. J. Schildknecht, Proc. 2nd Int.Symp.Loss Prev., Heidelberg (1977)