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Heat-flux calorimetric method for the determination of spontaneous oxidative heat rate of active carbon containing oxidizable/volatile organics[1]

Gene G. Wu*, David J. Leggett

Reactive Chemicals and Hazard Evaluation Laboratory, The Dow Chemical Company, Freeport, TX 77541, USA

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Abstract

Carbon beds containing organics, in contact with air, exhibit potential for thermal runaway. To accurately define the spontaneous oxidative thermokinetics, appropriate calorimetric techniques are required. A stopped-flow heat-flux calorimetry for oxidative heat-rate measurement is presented in conjunction with the results generated by accelerating rate calorimetry. The stopped-flow method eliminates many experimental uncertainties encountered with the conventional continuous gas-sparging method, and generates accurate and reproducible heat-rate data in a single test run. This technique is particularly useful in solid oxidation systems containing volatile organics.

Keywords: Activated carbon; Heat flux calorimetry; Thermokinetics

1. Introduction

Activated carbon containing oxidizable organic constituents, in common with porous, granular or fibrous high surface-area materials, may exhibit spontaneous oxidation or ignition behavior [1,2]. The use of activated carbon adsorption technologies, such as pressure swing adsorption, temperature swing adsorption and disposable canister absorber for solvent recovery and air pollution abatement, requires a thorough understanding of the oxidation kinetics of carbon loaded with volatile organics (VOCs). This knowledge furnishes the information necessary to understand the potential for runaway behavior and to provide the procedures required to manage that potential.

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* Corresponding author.

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Calorimetric techniques have been widely used for thermokinetic evaluation of active carbon oxidation potentials [3,4]. In general, three types of calorimetric techniques are used, including adiabatic, isothermal, and temperature-programmed calorimetry. It has been recognized that reactions having a small activation energy [5] or an autocatalytic nature [6] may result in the exotherm being detected at a higher temperature using temperature-programmed DSC or DTA than that using isothermal calorimetry.

Accelerating rate calorimetry (ARC) has been widely used for non-isothermal kinetic study of solid oxidations. However, due to its limited sensitivity, thermokinetic data obtained via this technique often require extrapolation to a lower temperature region. Factors such as complex reaction mechanisms [7], non-zero activation heat-content, autocatalytic reaction [5], and preceding equilibrium, can cause convex or concave ARC self-heat rate curves. These non-ideal curves make it impossible to use a linear or zero order extrapolation to provide heat rate data at lower temperatures. In the present study, this difficulty is encountered and circumvented by using the isothermal heat-flux calorimeter, which produces self-heat rate data at temperatures well below ARC detection limits.

Traditionally, to observe an oxidative reaction on an isothermal heat-flux calorimeter, air and nitrogen are alternately sparged through the sample cell. By measuring the heat rate difference between air and nitrogen sparging, an absolute oxidative heat rate could be determined. However, there are some technical limitations and difficulties for using this kind of gas-sparging method. For instance, the constant flow rates of air and nitrogen should be exactly equal to eliminate the heat effect due to different gas flow rates, and should be controlled at less than 1 ml min^{-1} to be thermally equilibrated. On the other hand, if the gas flow rate is too low, a diffusion controlled oxidation may be presented. Also, for solids containing volatile constituents, either over-saturation or under-saturation of the sparging gas with the volatile organics, will cause a non-equilibrium desorption

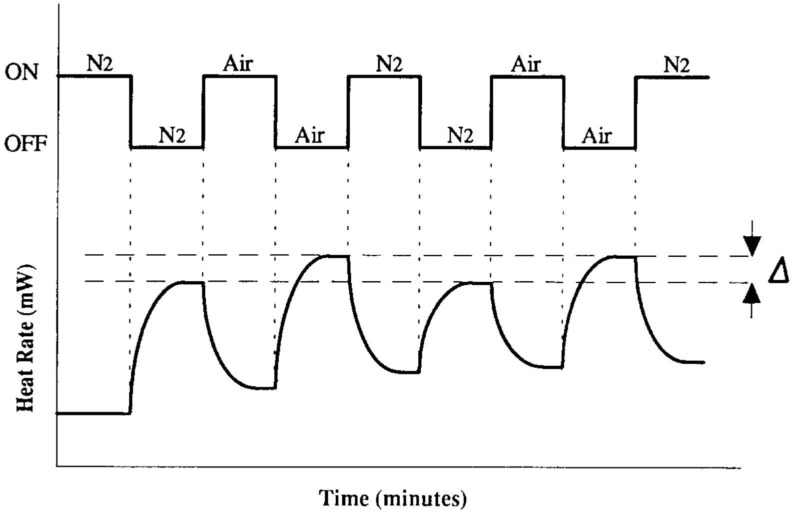

Fig. 1. An illustration of the stopped-flow method for heat rate measurements.

heat effect that may not be compensated for. Furthermore, the heat conductivity and heat capacity variations, due to non-equilibrium desorption by continuous gas sparging may result in a gradual heat rate change over time. This is particularly true when the volatile constituents could desorb from, or adsorb onto, the granular or powdered solids.

The stopped-flow (SF) technique introduced here simplifies the gas-sparging setup procedures and eliminates all of the above mentioned experimental uncertainties. The basic procedure of this technique is straightforward, as illustrated in Fig. 1. Data acquisition is started after an extended period of nitrogen sparging at the desired temperature in order to desorb the excess of volatile organics. Then, the air or nitrogen stationary condition of the carbon sample was perturbed alternately by nitrogen and air flows. The pulse width (Fig. 1) was normally set to 15–30 min. Since only the heat rate difference between the stationary or no-flow conditions (the top part of the heat rate curve) was to be measured, the bottom part of the heat rate pulse curves was without interest. Therefore, less effort was needed to control the gas flow rates. The method has also been found to be particularly useful in studying solid oxidation systems containing VOCs.

2. Experimental

The accelerating rate calorimeter, manufactured by Columbia Scientific Industries of

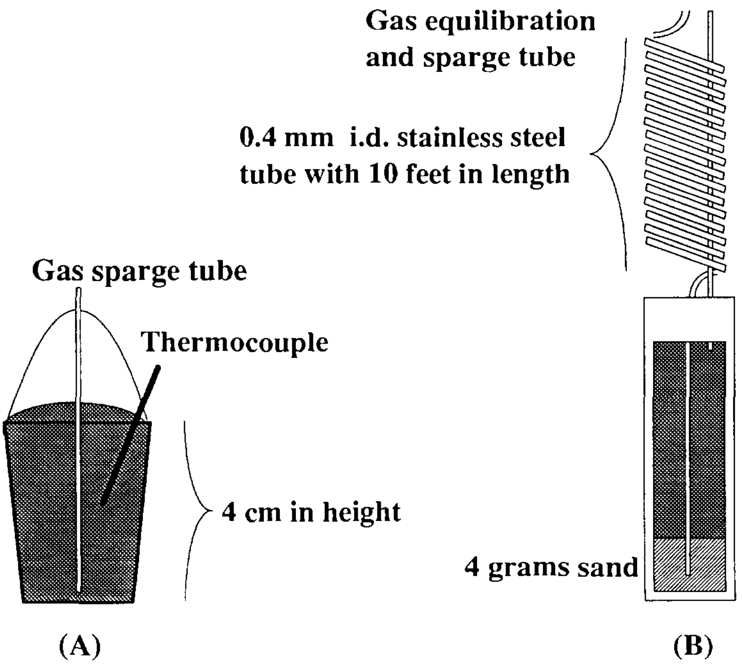

Fig. 2. ARC sparged-cell (A) and the modified C80 standard cell (B).

Austin, TX, under an abbreviated name CSI-ARC^{TM}, and the C80 heat-flux calorimeter, a modern type of Calvet microcalorimeter manufactured by Setaram of Lyon, France, were used for the present study.

The key to the operation of the sparged-cell ARC is the ability to maintain the adiabaticity of the sample system during gas sparging. To thermally equilibrate the incoming gas flow at exactly the same temperature as the sample system, an equilibration coil of a 1 mm i.d. stainless steel tube and a total length of about 5 m was placed inside the ARC adiabatic chamber, and the air flow rate was set to 1–2 cm^3 min^{-1}. To ensure that the air flow was evenly sparged inside the sample, the gas sparge tube was inserted onto the bottom of the sample mass, as shown in Fig. 2a. The sample cell with a total volume of about 15 ml was made of stainless steel thin foil with a stainless steel wire hanger. With this kind of sample system arrangement, a thermal inertia of less than 1.1 could be easily obtained. A sheathed Nisil/Nicrosil thermocouple was placed in the center of the sample mass.

Custom-designed gas flow cells (Fig. 2b) were used with the C80 heat-flux calorimeter. Inlet and outlet of gas flow tubes were welded onto the cap of the C80 standard cell. With the use of the SF method mentioned previously, gas flow rate control was no longer necessary, as long as the incoming gas flow was isothermal with the sample system. C80 calorimetric experiments were performed at 70, 90 and 130°C for the active carbon/ epichlorohydrin system. During the C80 experiment, before the SF procedure, each sample was sparged with nitrogen at the desired temperature for an extended period, until the heat flux signal change was minimized.

To convert heat rate into temperature rate, the following equation is used:

$$\frac{\mathrm{d}T}{\mathrm{d}t}\ (^\circ\mathrm{C\ min}^{-1}) = \frac{\mathrm{d}q/\mathrm{d}t\ (\mathrm{mW})(10^{-3}\ \mathrm{J\ s}^{-1}\ \mathrm{mW}^{-1})(60\ \mathrm{s\ min}^{-1})(\mathrm{cal}\ (4.184\ \mathrm{J})^{-1})}{Cp_{\mathrm{epi}}\,(\mathrm{cal\ g}^{-1}\ {}^\circ\mathrm{C}^{-1})m_{\mathrm{epi}}\ (\mathrm{g}) + Cp_{\mathrm{carbon}}\,(\mathrm{cal\ g}^{-1}\ {}^{\circ C}\mathrm{C})m_{\mathrm{carbon}}\ (\mathrm{g})}$$

where both Cp_{epi} and m_{epi} are temperature dependent and Cp_{carbon} is assumed to be temperature independent. Conversion of the self-heat rate units from mW to °C min^{-1} requires the knowledge of the heat capacity of the sample, consisting of the combined heat capacities of active carbon and the volatile organics, which can be measured or estimated.

All samples of active carbon (Calgon Carbon Corp.) with VOCs, were prepared according to the following procedures. A portion of granular active carbon was dried by being placed in a nitrogen-purged oven at 100°C for several hours, a given amount of the dried carbon was accurately weighed, soaked with the VOC solvent of interest, and then vigorously centrifuged to remove the excess liquid from the porous carbon particles. The maximum loading of VOCs on the granular carbon was typically 35–40 wt.% for VOCs, which is comparable to the amount of VOC loading by direct vapor adsorption.

The newly prepared VOC/carbon sample was placed in an ARC or C80 stainless steel vessel. The C80 calorimeter was ramped to the desired temperature in advance. The detection limit for ARC was set at 0.02°C min^{-1}, while the isothermal baseline noise of C80 was typically no greater than 10 mW. Immediately after the C80 experiment, the samples were weighed again and the residual loading of the volatile organics was determined.

This residual VOC is the actual equilibrium loading of the organic component and was used for the heat capacity calculation.

It should be mentioned that, theoretically and thermodynamically, there should be no difference between the samples prepared by direct vapor adsorption or by the above centrifuge method, if a reversible adsorption mechanism is assumed. This expectation was examined by using the ARC experiment against the samples with chloroform. It has been found that the heat rate difference between the samples prepared by the two methods was insignificant. However, if the volatile solvent contains a large amount of impurities or stabilizers, a difference in activation energy might be found.

3. Results and discussion

Fig. 3 summarizes the sparged-cell ARC auto-oxidation results for several chlorinated hydrocarbons. Isothermal self-heating rate data by C80 are plotted together with the ARC data in Fig. 4 for the epichlorohydrin/active carbon system. As illustrated in Fig. 2 and shown in Figs. 5–7, the net oxidative heat rates are easily defined and determined by drawing two parallel lines through the stationary oxidative and nitrogen plateaus.

From the ARC heat rate data, except from that of epichlorohydrin, the linear or Arrhenius kinetics could be easily defined, based on a zero order mechanism at the early conversion of the oxidative reaction. However, a convex-upward ARC heat rate curve was obtained for the active carbon/epichlorohydrin sample as shown in Fig. 4, making a linear extrapolation of the heat rate to a lower temperature impossible.

Linear or Arrhenius kinetics resulted from the heat-flux calorimetric experiments, i.e. the linear heat rate data of C80 in Fig. 4, indicating that a complex reaction mechanism or non-zero activation heat content was absent in the epichlorohydrin/carbon sample system. Also, as shown in Figs. 5–7 of the detected instantaneous heat of oxidation, the

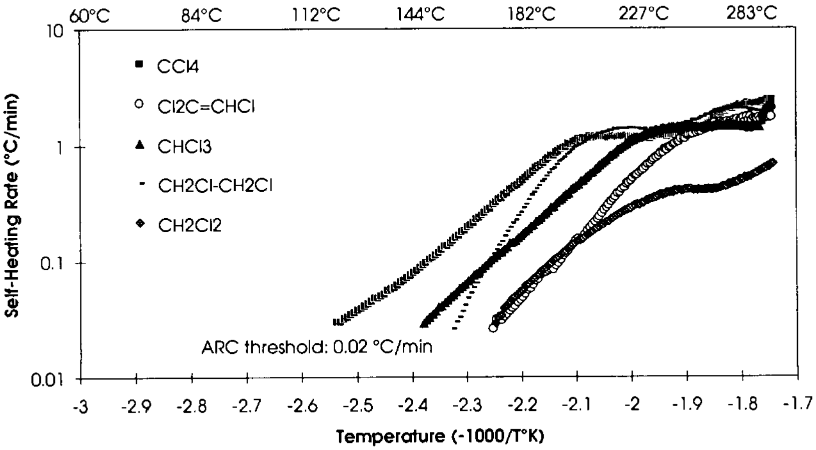

Fig. 3. ARC spontaneous oxidation heat rate curves of VOC carbon samples under air.

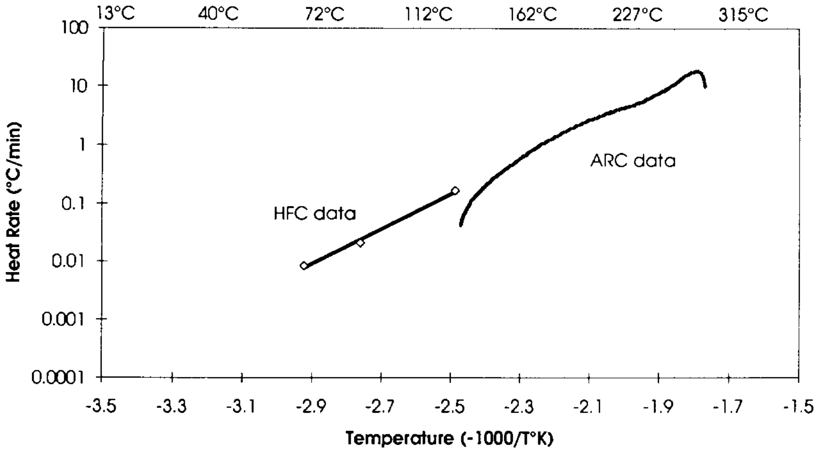

Fig. 4. Spontaneous oxidation heat rate curves, obtained on ARC and C80, of the epichlorohydrin-carbon sample under air.

time-dependent autocatalytic nature was also not observed. The reason why the non-linear ARC heat rate occurred in the epichlorohydrin/carbon sample system might be explained as the desorption of the excess epichlorohydrin from the active carbon particles, in the open-cell ARC testing system. Note that the detected temperature (130°C) for the exotherm on ARC is not far beyond the boiling point of epichlorohydrin (114°C). For the other VOCs, the detected temperatures for the exotherm on ARC (Fig. 3) are all well above their boiling points, and hence, such behavior was not observed. Based on these

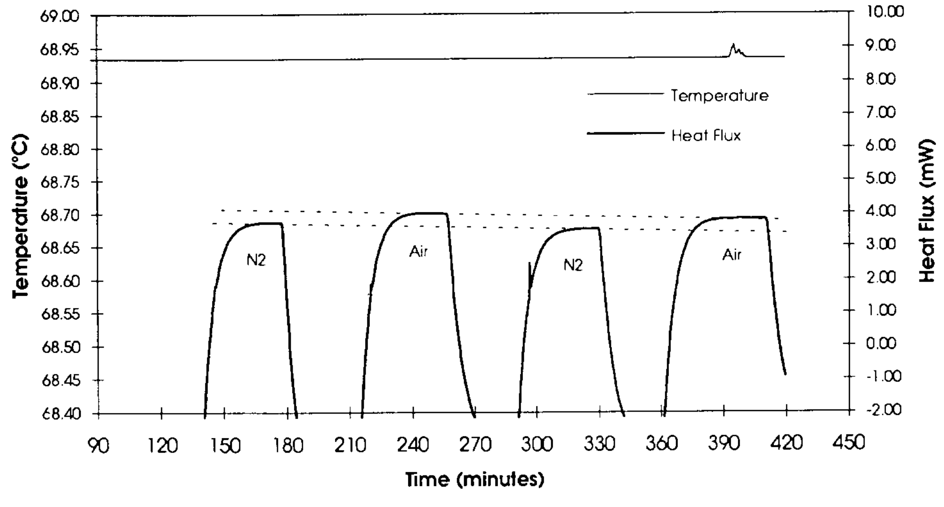

Fig. 5. Isothermal SF heat flux curve at 70°C of the epichlorohydrin-carbon sample.

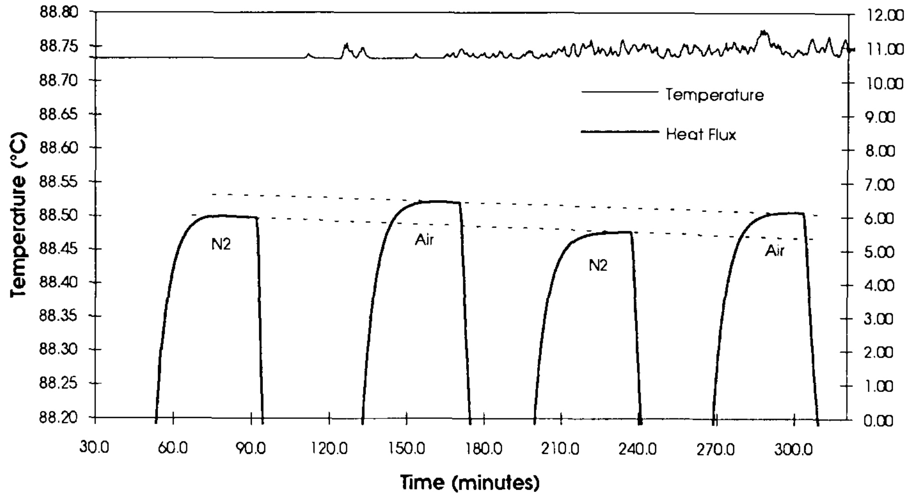

Fig. 6. Isothermal SF heat flux curve at 90°C of the epichlorohydrin-carbon sample.

observations, it might be concluded that the convex ARC heat rate curve of the epichlorohydrin system partly resulted from the overall heat rate balance between the spontaneous oxidation and the excess condensed phase evaporation. Also, the decrease of sample weight by evaporation might result in a significant decrease in sample heat capacity and hence a non-chemical heat rate increase over the temperature. However, with the temperature increases, these two factors become less and less evident. For the other chlorinated hydrocarbons, because the ARC detected temperatures of spontaneous oxi-

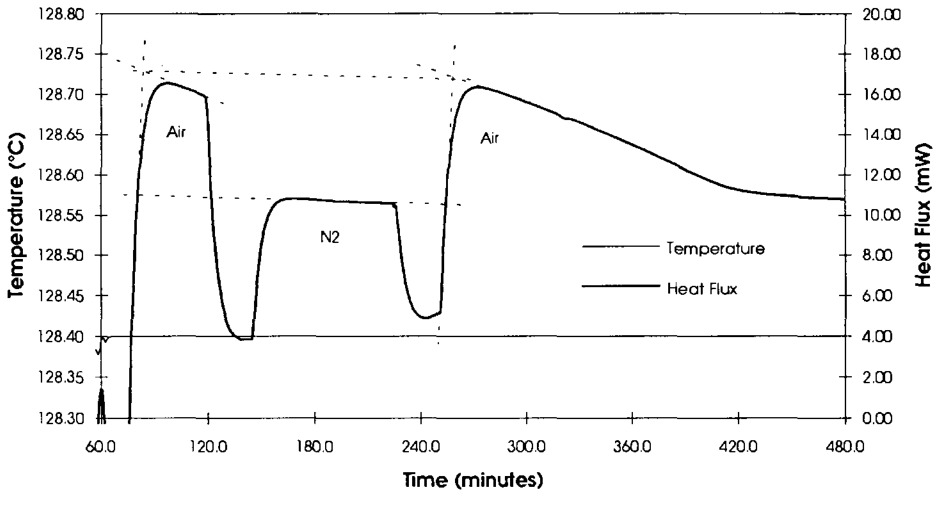

Fig. 7. Isothermal SF heat flux curve at 130°C of the epichlorohydrin-carbon sample.

dation were well above their boiling points, the desorption of the excess VOC from the active carbon particles was insignificant and non-linear behavior was not observed, as shown in Fig. 3.

In contrast, during the C80 experiments for the epichlorohydrin/carbon system, before the SF procedure, each sample was sparged with nitrogen at the desired temperature until the heat flux change was minimized. Since a no-flow condition was established in the relaxation steps of the SF procedure, the heat rate effects of desorption and heat capacity change were minimized. Therefore, a linear or zero-order heat rate curve over the experimental temperature range resulted (Fig. 4).

Caution must be taken in using the above calorimetric perturbation method. If the oxidative heat rate is larger than ca. 2 mW, as in the present study, an extrapolation might be needed in order to obtain the initial oxidative heat rate, as illustrated in Fig. 7. This is because the oxygen contained inside the cell is depleting at a rate of 0.2% per minute in the present experimental setup.

As demonstrated in the present study, the SF heat flux technique may be used as a standard calorimetric procedure to provide heat rate data throughout the actual, or close-to-actual, temperature regions of spontaneous oxidation of solids and/or solids containing volatile organics. In addition, it may be used as a quality control tool to verify the kinetic information generated by the conventional ARC technique.

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