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A DEVICE FOR SAMPLE AGITATION IN AN ACCELERATING RATE CALORIMETER

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ABSTRACT

A stirring bar type agitation system has been designed and characterized for the accelerating rate calorimeter (ARC). The device allows stirring of the contents of a standard ARC sample container at stirring rates of up to 500 rev. min^{-1}, depending on sample viscosity. Experiments on a well-characterized thermal decomposition reaction, such as that of di-*t*-butyl peroxide, indicate that the device does not degrade the measurement of the energy of reaction, ΔE_v, the Arrhenius activation energy, E_a, or the pre-exponential factor, A.

The utility of this stirring apparatus is demonstrated by examining the runaway data of a suspension polymerization. The results indicate that a polymerization "kill" agent can be successfully used for that particular reaction.

INTRODUCTION

Accelerating rate calorimetry has proved to be a useful technique in the evaluation of thermal runaway reaction hazards [1–4]. However, the accelerating rate calorimeter (ARC) is designed primarily for the analysis of homogeneous liquids. In order to achieve reliable results with the typical 1 in. diameter sample container, the sample must exhibit high thermal conductivity and/or low viscosity, which promotes free convective mass transfer. These sample characteristics are necessary so that both temperature and chemical concentration gradients are minimized during the experiment. Solid materials which do not melt prior to decomposition and samples containing multiple liquid phases which react with each other are examples of materials that may yield non-conservative results as to the runaway reaction hazards.

The utility of the accelerating rate calorimeter can be expanded with the addition of a small stirring device to the sample container. The approach taken in this work was to use a small stirring bar which is inserted into the sample container and can be driven by a cylindrical horseshoe magnet positioned just below the container. The implementation of this device has enabled this laboratory to examine the effect of agitation on heterogeneous samples in a limited fashion. The details of the instrument design, along with

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its advantages and disadvantages, will be presented in this paper.

In addition to the stirring capability, the accelerating rate calorimeter has been modified for the injection of small quantities of a second component directly into the sample at a specified reaction temperature. A liquid chromatographic septum injector valve can be used for this purpose. This modification of the ARC will also be discussed.

EXPERIMENTAL

The accelerating rate calorimeter (ARC) was developed by the Dow Chemical Company and licensed to Columbia Scientific Industries of Austin, Texas, which currently markets the instrument under the trademark CSI-ARC(TM). Since the details of the design, operation, and performance of the ARC have been published elsewhere [1–4], only a description of the instrumental modifications will be given here.

An illustration of the driving magnet is presented in Fig. 1. The cylindrical hoseshoe magnet is attached to a connecting drive shaft, which passes through a graphite bushing. The bushing is lightly press-fitted into a nickel sleeve, which, in turn, has been tightly press-fitted into a hole drilled through the base of the copper jacket. The nickel sleeve is used to prevent oxidation of the exposed copper surface at elevated temperatures. By nickel plating the copper jacket after the hole for the stirrer had been drilled, the nickel sleeve could be eliminated from this design. The graphite bushing serves as a bearing surface both under the magnet and on the drive shaft. The other end of the shaft passes through a brass bearing which is adjustable to allow alignment of the connecting drive shaft. This brass bearing is attached to the bottom of the standard calorimeter pot. A flexible drive shaft originating from a variable speed motor is attached to the end of the connecting drive shaft by means of a set screw and sleeve. Holes must be cut in the calorimeter mounting bracket (not shown) and the containment vessel (not shown) to accommodate the brass bearing and the flexible drive shaft, respectively. Note that, unless special provisions are made, the containment vessel can no longer be considered gas tight.

The cylindrical horseshoe magnet is available from Permag Central Corp., Elk Grove Village, IL 60007, part number 5U32B, cast ALNICO magnet. G.K. Heller Corp., Floral Park, NY 11001, supplied the following items: 2T60-1 variable speed motor, HT5-MR-AA-RN motor controller 0–1000 rev. min^{-1} max., and an A210 312 flexible drive cable.

Figure 2 illustrates the complete stirring assembly, modified pressure feed-through adapter, and septum injector port. An important design parameter, which can affect stirring efficiency, is the distance between the top of the horseshoe magnet and the bottom of the sample container. This distance is maintained between 0.10 and 0.15 in. (2.5–3.8 mm).

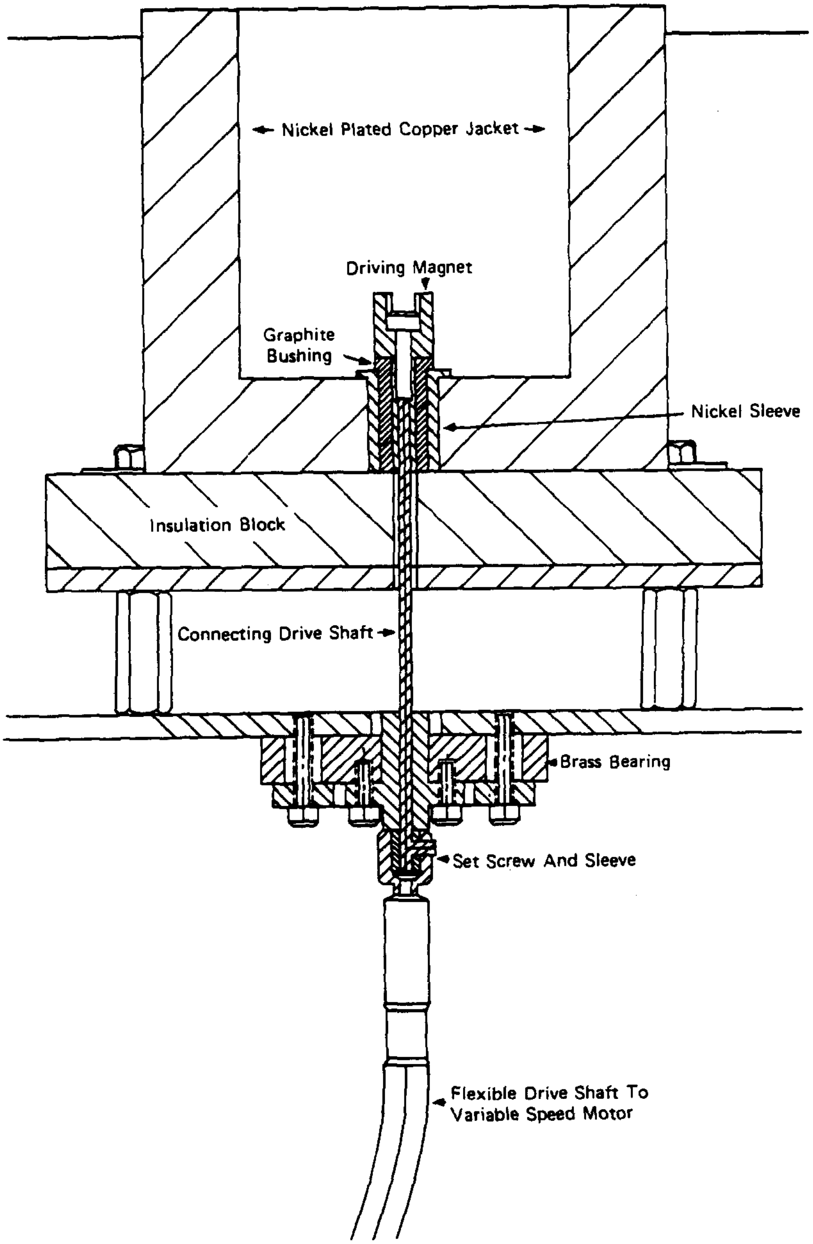

Fig. 1. Driving magnet assembly.

The small stirring bar coated with Teflon™, typically used with this design, measures 1.8 mm diameter × 8 mm long and is available from VWR Scientific, Inc., San Francisco, CA 94119, catalog number 58948-353. This stirring bar can be inserted through the 1/8 in. outside diameter × 0.085 in.

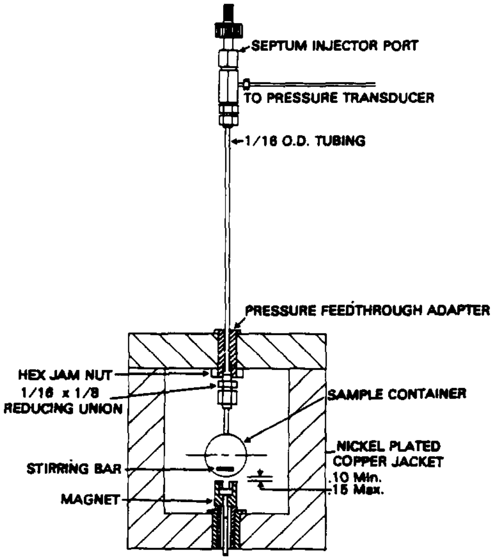

Fig. 2. ARC stirring bar agitator assembly with septum injection and pressure feed-through adapter.

inside diameter tube which is present on all light-weight titanium, Hastelloy C, and stainless steel sample containers.

The modified pressure feed-through adapter is a device which provides a low dead-volume, totally disposable connection between the sample container and the pressure transducer. It consists of a machined lid adapter for a 1/16 in. tubing union, a 1/8 × 1/16 in. tubing union, and a piece of 1/16 in. tubing. The machined lid adapter remains in the nickel-plated copper lid while the sample container, tubing union, and 1/16 in. tube are replaced after each experiment. A detailed drawing of this modified pressure feed-through adapter is available from the authors.

The straight-through septum injector valve shown in Fig. 2 is mounted in a "tee" configuration so that a syringe equipped with a long needle can be used to pierce the septum and inject material directly into the sample container which has been heated to any predetermined temperature. The septum injector valve is normally kept at room temperature. The valve is available from DuPont Instruments, Wilmington, DE 19898, septum injector port for model 848 liquid chromatograph, part number 848025901.

The viscosity standards used in this study were ASTM certified viscosity standard oils obtained from Cannon Instrument Co., State College, PA.

RESULTS AND DISCUSSION

In implementing instrument modifications, it is important to know the effect of the change on the performance of the instrument. Thermocouple noise and drift, coupling efficiency between the stirring bar and the horseshoe driving magnet, and the effect of the modification on model chemical systems are all subjects which are addressed in evaluating the characteristics of this stirring device. Unless otherwise noted, the following discussion applies to the stirring bar modification of the accelerating rate calorimeter as described in the experimental section of this report.

Noise and drift

The results of an experiment on short term noise related to turning rate of the driving magnet are presented in Table 1. Due to the configuration of the instrument, a changing magnetic field is produced in the vicinity of the sample container thermocouple when the magnet is turning. Therefore, the driving magnet is a potential source of electronic noise on the thermocouple circuitry. Thermocouple stability is of prime importance in the accelerating rate calorimeter since it directly affects instrument sensitivity. As is evident from the data of Table 1, the driving magnet has little effect on thermocouple noise even at high stirring rates. However, tests using a larger driving magnet did show substantial increases in short term noise.

The agitation of liquids is accompanied by an input of mechanical energy.

TABLE 1

Typical short term thermocouple noise as a function of stirring rate at 25°C using the cylindrical driving magnet in the absence of both stirring bar and liquid sample

	Stirring rate (rev. min^{-1})		
	0	300	1000
Peak-to-peak noise (°C)	0.02	0.02	0.03

TABLE 2

Calorimeter drift rate (°C min^{-1}) as a function of stirring rate and temperature

Data are corrected for observed drift at 0 rev. min^{-1}. Sample was 4.5 cm^3 H_2O with 1.5 mm × 8.0 mm Teflon-covered stirring bar

Temperature (°C)	Stirring rate (rev. min^{-1})					
	0	100	300	700	1200	2000
100	0	−0.003	−0.003	−0.001	0.000	+0.006
250	0	−0.002	−0.002			+0.011

Part of this energy appears as heat, which can cause a positive temperature drift in an adiabatic calorimeter. A study of drift rate as a function of both stirring rate and temperature was carried out and the results are presented in Table 2. The drift rates are very small up to 1200 rev. min^{-1} and cannot be attributed unequivocally to stirring. The drift rate appears to increase slightly at 2000 rev. min^{-1} at both 100 and 250°C. However, these drift rates are negligible for normal instrument operation since the detection limit of the instrument is usually set at 0.02°C min^{-1}.

Magnet separation distance, viscosity, and sample volume effects

Effective coupling between the driving magnet and the stirring bar in the sample container depends on several parameters, such as the actual distance between the driving magnet and the stirring bar, which determines the strength of the magnetic field used to drive the stirring bar, and the sample viscosity and the sample size, which represent a resistance to the stirring bar motion. Table 3 presents data on the effect of magnet separation distance and viscosity on the maximum stirring rate observed. As one might expect, the further apart the magnets are, the lower will be the maximum achievable stirring rate. The viscosity data show a maximum in the viscosity versus maximum stirring rate relationship which occurs at 33 cP. This phenomenon may be due to the size and shape of the sample container and their effect on the movement of the liquid mass inside. It should be noted that, since there are no baffles or irregularities in the interior of the standard sample container, the liquid tends to move as a swirling body with the vortex in the center. Although this is not an optimal situation, results presented later in this report indicate that rather efficient mixing of materials can be achieved with this design. One should also note that total loss of agitation does not

TABLE 3

Maximum stirring rate (rev. min^{-1})[a] as a function of sample viscosity and distance between sample container and driving magnet

The sample volume was 5 cm^3 in a 1 in. diameter glass sample container at 25°C

Distance between sample container and driving magnet (in.)	Viscosity (cP)				
	1	8	33	100	500
1/16	750	600	1800	600	50
1/8	500	550	900	250	None
1/4	400	500	600	150	None

[a] Maximum stirring rate is defined as the highest rate at which coupling still occurs between the stirring bar and the driving magnet regardless of how quickly the driving magnet is brought up to speed.

occur above the maximum stirring rates listed in Table 3. In reality, the decoupling of the stirring bar from the driving magnet causes the stirring bar to jump erratically in the sample container, resulting in some degree of agitation of the material.

To demonstrate the effect of sample size on the coupling of the magnets, an experiment was carried out where the sample volume was reduced from 5 to 2.5 cm^3 with a 1/16 in. separation distance. The test showed a maximum stirring rate of 500 rev. min^{-1}. This is a slight decrease from the 750 rev. min^{-1} observed for the 5 cm^3 sample listed in Table 3.

For normal instrument operation, the distance between the top of the driving magnet and the bottom of the sample container was chosen as 1/8 in. as illustrated in Fig. 2. All the subsequent data found in this report were generated under this condition.

In order to show that the above data are also valid for the typical metal sample containers used in an accelerating rate calorimeter, tests were carried out in both Hastelloy C and titanium containers in which a small window had been machined near the container stem for observing the stirring activity. The data of Table 4 can be compared with those of Table 3 to demonstrate that the metal containers perform in a manner similar to the glass container. One might note that the maximum stirring rate for a 33 cP fluid is somewhat less in the metal containers. This may be due to the difference between the spun metal and glass surface roughness or resistance to fluid flow.

The above results have been utilized in this laboratory to set guidelines on stirring rates for routine analyses. For low viscosity liquids, 500 rev. min^{-1} appears to be a reasonable upper limit on the stirring rate, while 200 rev. min^{-1} might be the maximum for a medium viscosity liquid (50–100 cP). Above 100 cP, it is doubtful that any significant agitation of the fluid can be

TABLE 4

Maximum stirring rate (rev. min^{-1})[a] as a function of sample viscosity in a metal sample container

Sample volume was 5 cm^3 with container to magnet distance of 1/8 in.

Sample container	Viscosity (cP)		
	1	8	33
Hastelloy C	700	700	1100
Titanium	600	700	1100

[a] Maximum stirring rate is defined as the highest rate at which coupling still occurs between the stirring bar and the driving magnet regardless of how quickly the driving magnet is brought up to speed.

effected with this stirring bar device. These guidelines apply to room temperature and do not take into account temperature dependence of viscosity or the formation of reaction product(s) which either exhibit increased or decreased viscosity.

Model chemical system, di-t-butyl peroxide

When making modifications to an instrument, it is important to know what effect, if any, the change has on the behavior of a well-characterized chemical system. In this case, di-*t*-butyl peroxide was chosen as the model compound, since its reaction has been studied previously in the accelerating rate calorimeter [3], and the addition of a stirring device was not expected to affect the thermodynamics or kinetics of the reaction. The experiments involved three separate instruments. Instrument A was the unmodified accelerating rate calorimeter. Instruments B and C were calorimeters which had been modified with stirring bar type agitation as described in the experimental section. The experiments carried out on instruments B and C were run both with and without stirring of the contents of the sample container. When non-stirred experiments were run on these latter two devices, only the stirring bar was omitted, the driving magnet remained in place, although it was not rotating. Two or three replicates were run under each set of experimental conditions using a 20% solution of di-*t*-butyl peroxide in toluene.

The effect of the stirring bar modification on the energy of reaction at constant volume, ΔE_v, was the first experimental result to be examined in this study (see Table 5). The data indicate that, for stirred vs. unstirred experiments, only one of the two calorimeters equipped for agitation, B and C, showed any deviation in the observed ΔE_v and that was a small effect, viz. 0.9 kcal mole^{-1} for calorimeter C. A much larger effect was evident between the calorimeters A, B, and C. Taking the results from calorimeter A as the basis for comparison, calorimeter B with stirring yielded results 8.5% low, while calorimeter C with stirring appeared to be 3.9% low. Since the expected relative precision based on one standard deviation (1σ) of the unmodified instrument is 7.7% for the measurement of ΔE_v [3], the data indicate that the modification does not grossly affect the calculation of ΔE_v. In order to quantitate the effect of the modification on the data, a much more complete statistical evaluation would be necessary which would involve many different calorimeters. The above results can be referenced to 40.6 ± 1.8 kcal mole^{-1} as measured by differential scanning calorimetry [3].

The Arrhenius activation energy, E_a, and the pre-exponential factor, A, were calculated from the same experimental data used to evaluate ΔE_v in Table 5. The kinetic data are compared with the results from a previous study on di-*t*-butyl peroxide in the accelerating rate calorimeter by Tou and Whiting [3]. The results from calorimeters A and C, with and without

TABLE 5

The effect of the stirring bar modification on ΔE_v, E_a, and $\log A$ for three separate calorimeters

The sample was 5 cm^3 of 20% di-*t*-butyl peroxide in toluene in a titanium sample container; ϕ ranged between 1.55 and 1.60 [a]

Instrument	Modified	Stirring	Replicates	ΔE_v (kcal $mole^{-1}$)	Average E_a (kcal $mole^{-1}$)	Average $\log A$ (log sec^{-1})
A	No		2	-41.1 ± 0.1 [c]	38.8	16.59
B	Yes	No	3	-37.8 ± 1.5	39.3	16.93
B	Yes	Yes	2	-37.6 ± 0.3	39.2	16.89
C	Yes	No	2	-40.4 ± 1.4	37.9	16.18
C	Yes	Yes	2	-39.5 ± 0.9	37.0	15.67
Tou et al. [b]	No			-40.6 ± 1.8 [d]	37.80 ± 1.1	16.15 ± 0.61

[a] $C_{vs} = 0.5$ cal g^{-1} $°C^{-1}$; $C_{vb} = 0.13$ cal g^{-1} $°C^{-1}$.

[b] Results are from 12 runs on varying concentrations of di-*t*-butyl peroxide in one calorimeter. Precision is based on one standard deviation (1σ) value for those runs [3].

[c] Error reported is observed experimental data range.

[d] DSC measurements [3].

stirring, fall within the 1σ precision limit found in the previous study. The data from calorimeter B are consistent with each other but appear to fall slightly outside the 1σ precision range. These data indicate that the stirring bar modification to the accelerating rate calorimeter does not adversely affect the kinetic data acquired for this chemical system beyond that which would be expected due to run-to-run and calorimeter-to-calorimeter differences on unmodified calorimeters.

Agitation-sensitive reaction-suspension polymerizations

Suspension polymerizations are typically dependent on agitation to achieve proper particle size and to effect proper distribution between the aqueous and organic phases of the various chemicals in the system. Figure 3 contains the accelerating rate calorimeter data on a styrene/divinylbenzene suspension reaction initiated with organic peroxides. The aqueous phase contains a suspending agent and a stabilizer. The total reaction mixture is about 60% organic and 40% aqueous. The uppermost curve in Fig. 3 illustrates the results on this reaction mixture with stirring bar agitation at 500 rev. min^{-1}.

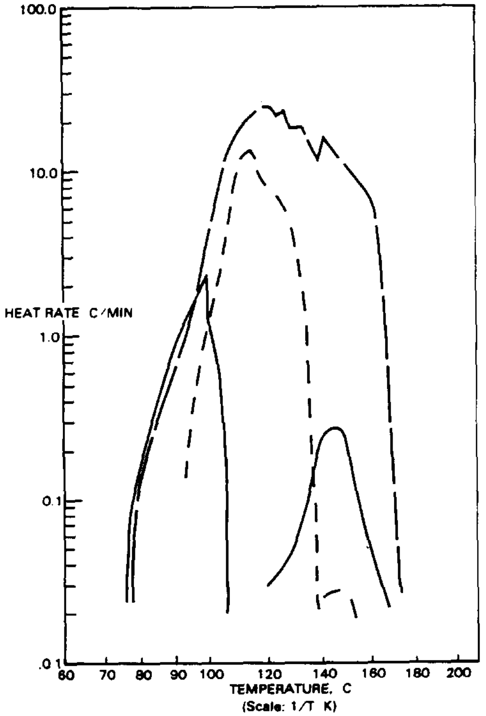

Fig. 3. ARC data on a suspension polymerization reaction. — — —, Stirring bar agitation; ——, stirring bar agitation with shot addition of Pennstop^{TM} at 100°C; - - - - - -, no agitation with shot addition of Pennstop^{TM} at 100°C.

Since a significant amount of heat can be generated at fairly high rates from this reaction, it was hoped that an initiator-kill or free radical scavenger could be found which, when added to the runaway reaction at 100°C, would stop or control any further polymerization and prevent the venting of the reactor contents. Pennstop^{TM} (Pennwalt Corp.), which is *N*,*N*-diethylhydroxylamine, is a common initiator-kill agent. The solid line of Fig. 3 shows what happens to the reaction when Pennstop is added to the reaction mixture at 100°C. Approximately 30 μl of Pennstop was injected into the sample container using the septum injector device described in the experimental section of this report. As one can see from the data, the addition of this material rapidly quenches the polymerization reaction. The data also show that the temperature must be raised to nearly 120°C in order to cause polymerization to recur at any appreciable rate. The heat that is generated above 120°C presumably arises from the thermally initiated polymerization of the residual monomers.

In order to demonstrate the importance of agitation in the previous two experiments, a run was carried out with no stirring of the reaction mixture. The results are presented as the short broken line of Fig. 3. Without agitation, both heat and mass transfer are affected in the sample to such an extent that the normal initiated polymerization is not detected until nearly 95°C, considerably higher in temperature compared with the experiments where agitation was present. Pennstop was injected at about 100°C as before but, in the absence of stirring, the Pennstop does not appear to mix sufficiently with the reaction mixture to quench the polymerization at 100°C. It does, however, seem to slow the reaction down somewhat above 125–130°C.

CONCLUSIONS

Not only has the development of agitation in the accelerating rate calorimeter permitted our laboratory to evaluate thermal reaction hazards for suspension polymerization systems, it has also proved to be of great value for other multiphase reaction systems such as emulsion polymerizations, interphase reactivity of two and three phase tar streams, and aluminum reactivity with chlorinated solvents and pesticides.

FINAL CAUTION AND LIMITATIONS

One should always realize that this stirring device can only provide a limited amount of agitation to the sample and because of this fact, the data may not be conservative in heat generation rates observed. Great care should be exercised in relating data generated using this technique to large scale plants and processes. Both the temperature limits of the coating of Teflon^{TM} on the stirring bar and the loss of magnetic force with temperature should be considered when utilizing this modification.

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