MASTER

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ENERGIES OF ORGANIC COMPOUNDS

Progress Report
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NOTICE

Abstract

Two automated reaction calorimetry systems are being constructed. The first, using a quartz thermometer probe, is essentially complete, and has been tested. It gives a precision of ± 50μ° in temperature measurement. The second uses a high precision digital voltmeter coupled to a microprocessor, and measures the resistance of a thermistor. Preliminary results indicate a precision of ± 100μ° in temperature measurement. The advantage of the second system lies in the small size of the temperature probe.

The calorimeter systems have been used in measuring the heat of hydration of orthoesters which is a model for the steric effects in converting a tetrahedral carbon to trigonal. It has been used to measure the heat of adding trifluoroacetic acid to alkenes. This reaction is useful for the determination of the difference in heats of formation between isomeric alkenes, the heats of hydration of alkenes, and the heats of formation of secondary and tertiary alcohols. It has been used in measuring the heat evolved in adding acetic acid across strained carbon-carbon single bonds.

Progress Report

One of the first goals of our investigation was the development of automated systems for reaction calorimetry. This was needed if we were to attempt to obtain any reasonably large bodies of data. The first system is about 95% complete. It utilizes an Intel 8080 microprocessor and a set of 35 MHz counters which monitor the frequency of Hewlett-Packard quartz thermometer probes. We have constructed the required preamplifiers and signal conditioners which convert the oscillator output into TTL level pulses. The counters were constructed using 74120 data synchronizers as the input device. In this way, the counters were made to totally integrate the input pulse stream, and eliminate the quantization error usually associated with counters.

Control devices were added to permit the microprocessor to cause the ampoule to be broken at the start of the reaction, to cool the reaction vessel back to the original temperature at the end of a run, and to effect an electrical calibration. As the calorimeter run or electrical calibration is being carried out, the temperature in the reaction vessel was measured once each 10 sec, stored in semiconductor memory, and printed using a small (40 column) line printer. At the end of a run, the data are punched on paper tape. The remaining part of this system is an interface to a larger computer so that the data may be transferred directly, rather than via paper tape.

Programs have been written for reducing the data and giving the heat of reaction.

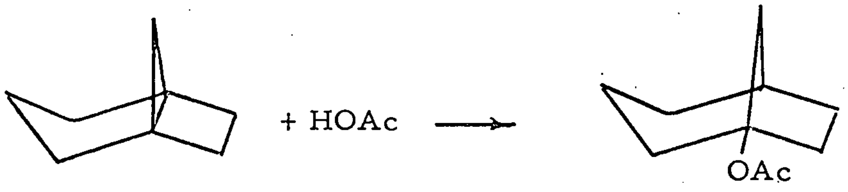
The system has been tested using two reactions. The first is the standard reaction for reaction calorimetry, that between TRIS and 0.1N hydrochloric acid. The time-temperature data for the foreperiod or the afterperiod could be fit with an rms error of 50μ°, indicating the system to be both very stable and very precise. The heat of reaction was found to be -7114 ± 11 cal/mole, as compared to the generally accepted value of -7115 ± 7 cal/mole. We are well satisfied with its performance.

The system was used to study the acid catalyzed hydrolysis of methyl orthoacetate to methyl acetate. The reaction is essentially instantaneous and thus is ideal for reaction calorimetry. The heat of reaction was found to be -6459 ± 9 cal/mole. The very low experimental error indicates that the entire system performs extremely well. We are now ready to use it to study the heats of hydrolysis of a series of orthoesters, ketals and acetals.

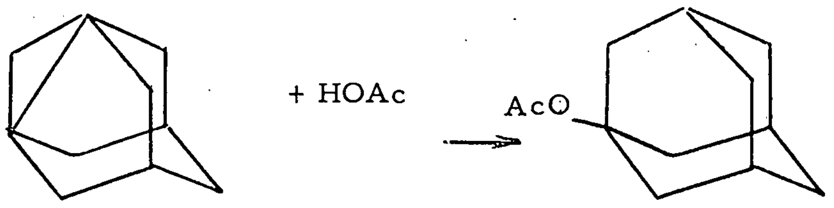
The one disadvantage of the calorimetric system results from the relatively large size of the quartz thermometer probes. This restricts the reaction cells to a volume on the order of 100 ml. The temperature sensor which is best suited to small cells is the thermistor. In order to be able to make use of these devices, a second calorimetric system is currently being constructed and is approximately 70% complete. It makes use of a PDP-11/03 microprocessor as the control device and a Fluke model 4500 digital voltmeter as the resistance measuring device. With relatively high resistance thermistors (~ 10,000 ohm), the voltmeter is capable of measuring the resistance with a precision of ±0.01 ohm. The calorimetric vessels designed for the LKB calorimeter use a 2000 ohm thermistor. The direct measurement of this resistance leads to excessive self-heating because of the current used (1.25 ma vs 75 μa for the 10,000 ohm range). A separate circuit was built which permits a current of 0.3 ma to be used and the resistance to be determined by measuring the voltage across a standard 2000 ohm resistor and then the voltage across the thermistor. Preliminary runs using this system indicates that temperatures can be determined with an error of ±0.0001°. This is not quite as good as is possible with the quartz thermometer, but it is very adequate for reaction calorimetry.

The circuits for automatically carrying out the electrical calibration, and for performing the other operations necessary in order to obtain the heat of reaction are being constructed. The apparatus is nearly complete and requires mainly the delivery of a few integrated circuit chips. It is expected that the entire apparatus will be ready for final testing by the end of July.

The following calorimetric measurements have been made:

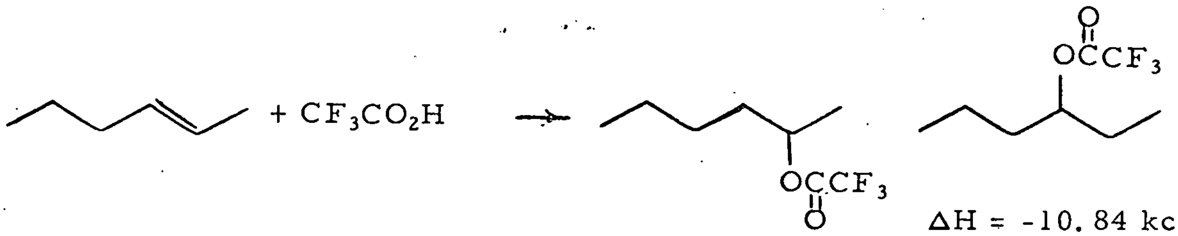


$\Delta H = -41.2 \pm 0.2$



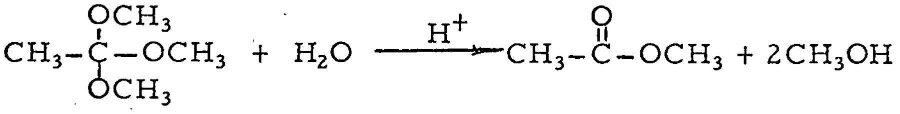
$\Delta H = -43.3 \pm 0.2$

This is the beginning of a series of measurements designed to determine the degree of strain relief which is possible by the cleavage of a single bond. Also:



$\Delta H = -10.84$ kcal/mole

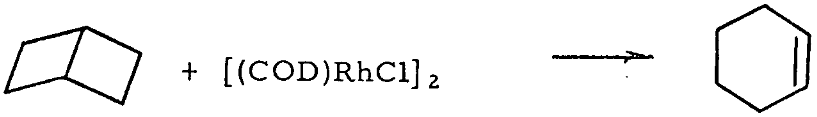
This is a test case for a series of measurements designed to give differences in heats of formation between isomeric alkenes, and the heats of hydration of alkenes. The reaction is quite rapid and well suited to reaction calorimetry. As mentioned above, we have also examined the following reaction and have found it to be well suited to reaction calorimetry.



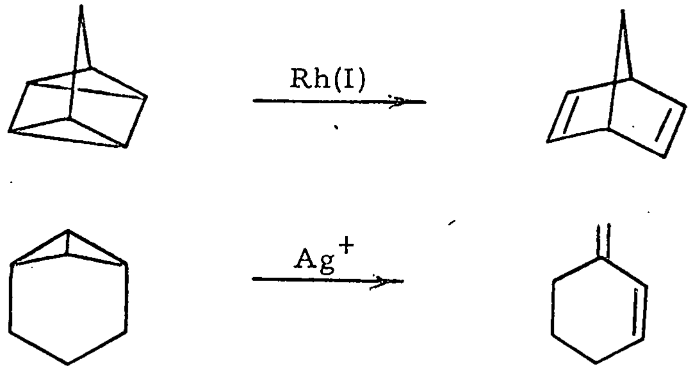
$$CH_3-\underset{OCH_3}{\overset{OCH_3}{C}}-OCH_3 + H_2O \xrightarrow{H^+} CH_3-\overset{O}{\overset{\|}{C}}-OCH_3 + 2CH_3OH \qquad \Delta H = -6.46 \text{ kcal/mole}$$

This is part of a series of planned measurements designed to determine the steric effects associated with the conversion of a trigonal carbon to tetrahedral, or vice-versa.

Many of the systems of interest contain cyclobutane rings which are not easily opened by chemical reagents. We have worked on the problem of finding a catalyst which would lead to a rapid reaction at room temperature, and one was found



Many other catalysts were tried, but this was the most effective. It still is not truly catalytic since some change in the rhodium occurs. However, it is sufficiently promising so that further work is planned. If the reaction can be made purely catalytic, it will allow the heat of the reaction to be determined, and this combined with the heat of formation of cyclohexane would give the heat of formation of the bicyclo[2.2.0] hexane. Other systems which we have successfully studied are



These studies will provide data on the heats of formation and strain energies of highly strained compounds. Some of these compounds, such as quadricyclane, have been proposed as energy storage media, and it should be helpful to have precise calorimetric data for their heats of reaction.