

10 cc./mole is used to decide between two possible reaction mechanisms. More accurate determinations of activation volumes would also allow estimation of certain properties of the activated complex. For example, measurement of the solvent effect on activation volume has been used to estimate the dipole moment of the activated complex by Heydtmann, Schmidt, and Hartmann (10) for a Menschutkin reaction. Very accurate data are also required for determination of the compressibility of the activated complex. Finally, changes of only a few cubic centimeters in activation volume often yield useful information about the solvent-complex intermolecular forces, which can in turn be most useful in designing solvents or solvent mixtures for a reaction (5).^o

THE EFFECT OF TEMPERATURE RISE FROM COMPRESSION

A major difficulty in previous high pressure kinetic measurements has been the increase in temperature which occurs when the reaction mixture is compressed. The temperature rise produced by an adiabatic compression is given by

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T}{C_P} \left(\frac{\partial V}{\partial T}\right)_P \quad (2)$$

For most organic liquids, the rise in temperature caused by adiabatic compression is 15° to 20°C. for the first 1,000 atm.

To estimate the effect of compression heating on the rate constant, measurements of the temperature rise and decay in a reaction cell under pressure have been made. A copper-constantan thermocouple was placed inside a Teflon reaction cell, which was filled with acetone, placed in a steel high pressure vessel, and immersed in a pressure transmitting fluid which was 50% kerosene and 50% SAE 10 oil. The pressure vessel was sealed and immersed in a temperature bath held at 35.00° ± 0.02°C. After temperature equilibrium had been attained, the pressure was increased at a rate of 1,000 atm./min. The increases in temperature inside the reaction cell ranged from approximately 15°C. at 1,000 atm. to 36°C. at 3,000 atm. The half-life for temperature decay increased from approximately 3.0 min. at 1,000 atm. to 4.5 min. at 3,000 atm.

In several previous studies, some attempt has been made to compensate for heating caused by compression. Coillet and Hamann (4) precooled the reaction mixture to -32°C. to measure the rate constant for an aromatic nitration at 0°C. and 2,000 atm. Brower (3) made a blank run at each pressure for ½ hr. The most common procedure has been to raise the pressure gradually to reduce the initial temperature rise. However, raising the pressure too slowly causes a large uncertainty in the starting time. Therefore, compression rates have been on the order of 1,000 atm./min. (15).

Calculations of the effect of an initial temperature elevation on the rate constant have been made for a typical example, an equimolar second-order reaction with a reaction half-life of 4 hr. It was assumed that the temperature followed a simple exponential decay. Calculations were made for temperature half-lives of 3 and 5 min. The rate constant was assumed to follow the Arrhenius expression. The bath temperature T_0 was chosen to be 35°C.

Temperature at any time t is given by

^o Recently this technique has been applied quite successfully to mechanism determination for several Diels-Alder reactions [Grieger, R. A., and C. A. Eckert, *J. Am. Chem. Soc.*, 92, 2918 (1970)]. Also, for the isoprene-maleic anhydride addition, solvent effects on the activation volume have been measured and used to determine various properties of the transition state [Grieger, R. A., and C. A. Eckert, *Trans. Faraday Soc.*, 66, (1970)].

$$T = T_0 + (T_1 - T_0) e^{-c_1 t} \quad (3)$$

where $(T_1 - T_0)$ is the initial temperature elevation. The rate constant at any temperature is given by

$$k_x = k_{x0} \exp \left[\frac{-E_A}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (4)$$

Activation energies of 10 to 30 kcal./mole were used in the calculations.

The equimolar second-order rate expression is

$$\frac{dx}{dt} = -k_x x^2 \quad (5)$$

In this case, k_x is a function of time, determined by Equations (3) and (4). Equation (5) was integrated with a third-order Runge-Kutta method, with an interval size of 0.01 hr. used. The apparent rate constant k_a that would be determined by measuring x and by assuming k_x constant in Equation (4) (that is, by assuming that the temperature rise was negligible), has been calculated. This is compared with the actual rate constant which one desires to measure, k_{x0} , the rate constant at the bath temperature T_0 . These results, as a function of time, are shown in Figures 1 and 2. An initial temperature rise on compression of 20°C. has been assumed. It can be seen that the error in the rate constant can be significant even for relatively large times.

THE IN SITU MIXING TECHNIQUE

The possibility of using some technique for mixing reactants under pressure after the heat of compression has been dissipated has been mentioned in reviews by Le Noble (11) and Whalley (16). The first technique ever reported for starting a liquid-phase reaction in situ under pressure is reported in this work.

In conjunction with the mixing technique, it is convenient to use some method for withdrawing samples for analysis without interfering with the reaction. More data points can be obtained from each experimental run, and the time uncertainty associated with opening the bomb to remove the reaction mixture for analysis is eliminated. Sampling in this work has been performed at pressures up to 6,120 atm.

Two types of reaction cells were used. At the lower pressures a Teflon cell, as shown in Figure 3, was employed, and the Teflon-to-Teflon seal of the pistons in the cylinders was satisfactory. At higher pressures (above about 1,500 atm.) deformation of the Teflon resulted in leaks and experiments were done in a nonmagnetic stainless steel

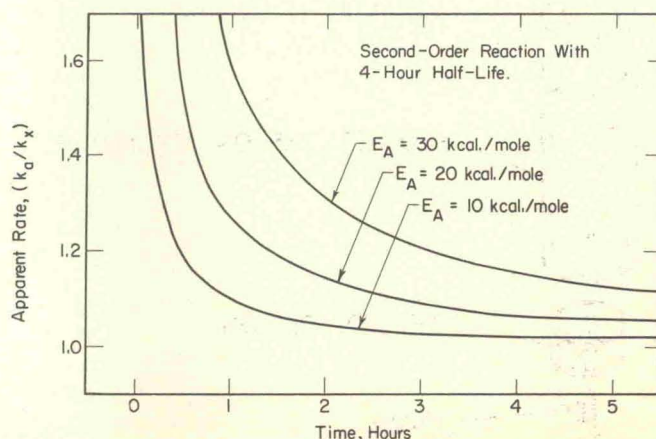


Fig. 1. Effect of an initial temperature rise of 20°C. on the measured rate constant. Temperature half-life = 3.0 min.

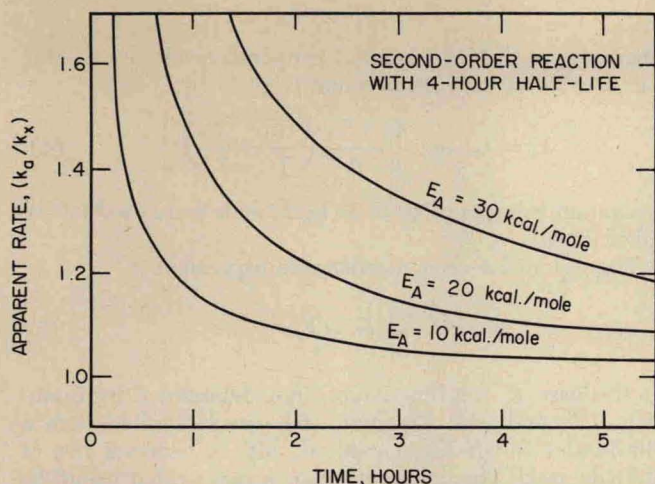


Fig. 2. Effect of an initial temperature rise of 20°C. on the measured rate constant. Temperature half-life = 5.0 min.

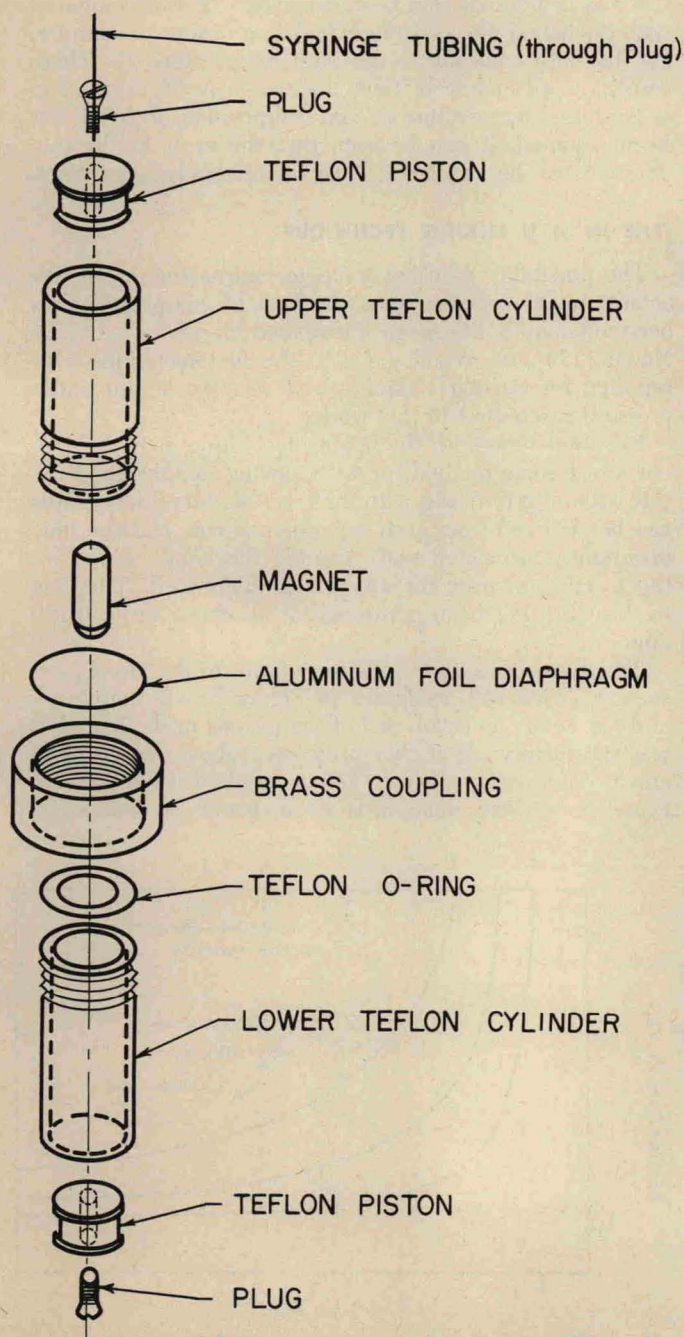


Fig. 3. Expanded drawing of reaction cell.

cell, identical to the Teflon one except that the piston-to-cylinder seal was by an o-ring.

Because ordinary rubber o-rings swell in organic liquids and freeze the pistons, o-rings of CNR nitroso rubber were used. This rubber is exceptionally inert and resistant to swelling (9). The o-rings were covered with a single layer of Teflon tape to reduce friction with the walls.

The center hole in each piston was drilled and tapped for a 6-32 machine screw. The cell is loaded by injecting solutions of reactants through these holes and by sealing them with screws covered with Teflon tape. To connect the cell to the syringe tubing used for sampling, a screw with a hole drilled through the center is soldered to the lower end of the syringe tubing and inserted in the upper piston. The cell is then suspended from the syringe tubing and free to move as the liquid inside is compressed.

Before the reaction is started, a Teflon covered magnet rests on the aluminum foil diaphragm, which is 0.00045 in. thick. Hydrostatic pressure can be applied without rupturing the foil. After thermal equilibrium has been reached, the reaction can be initiated by breaking the foil with the magnet and by mixing the solutions of the reactants.

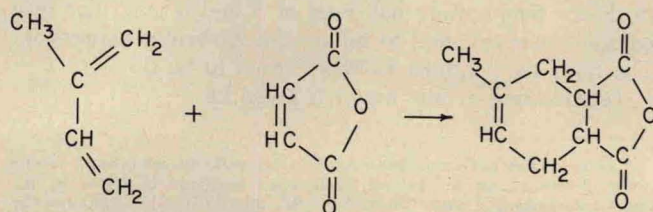
It was found that merely lifting the magnet and dropping it was insufficient to break the foil. Two overlapping coils were wound on the cell, one near the top and the other around the middle. The coils were constructed of No. 32 enameled copper wire at approximately 500 turns/in. By applying a sequence of direct current pulses, the magnet can be lifted and then accelerated toward the foil. After the foil is broken, the magnet is moved up and down to mix the reactants. One can tell when the foil is broken by measuring the change in inductance of the coil when the magnet breaks through and drops to the bottom section of the cell.

The foil breaks after being hit seven to ten times with the magnet. Twenty additional stirring cycles give adequate mixing. The increase in temperature from electrical heating is less than 0.5°C.

Although the in situ mixing technique is described here for a reaction followed by sampling and gas chromatographic analysis, it is by no means so limited. Samples could be taken for analysis by other analytic techniques, such as spectroscopy, pH measurement, or even titration if not too large a sample were required. The mixing technique has also been applied to a situation where analysis was carried out in situ by direct conductivity measurements (14).

THE ISOPRENE-MALEIC ANHYDRIDE CONDENSATION

The Diels-Alder reaction was selected for study because it is an uncomplicated bimolecular reaction of considerable experimental and commercial importance. The Diels-Alder reaction involves the 1,4 addition of a conjugated diene to a double bond or to a triple bond with formation of a six-membered ring. The reaction of isoprene and maleic anhydride is a typical Diels-Alder reaction and was studied in this work:



A schematic drawing of the high-pressure equipment is shown in Figure 4. The high pressure bomb was of single