

M = molecular weight
 Mai = local isothermal Mach number
 \overline{Mai} = average isothermal Mach number for cross section
 N_{Re} = Reynolds number
 P = pressure
 R = perfect gas law constant
 r = radial distance
 T = absolute temperature
 U = local axial velocity
 \overline{U} = average axial velocity for cross section
 $\overline{U^2}$ = mean square axial velocity for cross section
 V = radial velocity
 μ = viscosity
 ρ = density
 τ_w = local wall shear stress
 $\bar{\tau}_w$ = average wall shear stress for given length of tube

Subscripts

0 = at center line
 1 = upstream tap
 2 = downstream tap

LITERATURE CITED

1. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," p. 211, Wiley, New York (1960).
2. Dodge, B. F., "Chemical Engineering Thermodynamics," p. 350, McGraw Hill, New York (1944).
3. Dushman, S., "Scientific Foundations of Vacuum Technique," 2 ed., p. 82, Wiley, New York (1962).
4. Kuo, Y. H., *J. Math Phys.*, **22**, 13-30 (1943).
5. Langhaar, H. L., *Trans. Am. Soc. Mech. Engrs.*, **64**, A-55 (1942).
6. Shang, J., and M. H. Bloom, *Polytechnic Inst. of Brooklyn Aeronautical Lab. Rept. No. 749* (May 1962); N62-13611 Ad278 128.

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A New Technique for Chemical Kinetics at High Pressures

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Information about the transition state of a chemical reaction is quite useful for the determination of mechanisms and for design of solvents for the reaction. High pressure kinetic studies, if sufficiently accurate, provide the required data. This work reports a new technique developed for measuring rates of chemical reactions in solution at high pressure. This method involves in situ mixing of reactants under pressure and direct sampling for analysis, eliminating large errors of temperature equilibration and time measurement inherent in existing techniques, and thus yielding more accurate results. Experimental results for the Diels-Alder reaction of isoprene and maleic anhydride are reported at pressures up to more than 6,000 atm.

A new technique for high pressure chemical kinetics has been developed for very precise determinations of volumes of activation. By eliminating two sources of significant uncertainty inherent in previous methods, errors in time and temperature, activation volumes may be measured with an accuracy better than 1 cc./g.-mole. The technique proposed here includes the first reported application of in situ initiation of the reaction, avoiding errors in temperature due to the heat of compression or the thermal lag of a heavy steel vessel. Analyses were carried out by continual sampling, at pressures more than twice as high as those at which previous high pressure sampling had been reported (7, 11), permitting much more accurate time measurements than would be obtained by the classical method of disassembly of the vessel for analysis.

The effect of pressure on the rate of a chemical reaction yields important information about the structure and properties of the transition state for the reaction. The activated

complex theory of Evans and Polyani (6) provides a theoretical basis for interpretation of high pressure kinetic data. Using this approach, and expressing the rate constant in pressure invariant concentration units (such as the rate constant in mole fraction k_x), one may show rigorously (8) that the measured effect of pressure gives the volume of activation ΔV^\ddagger , the difference in partial molal volume between the transition state for the reaction and the reactants:

$$\left(\frac{\partial \ln k_x}{\partial P} \right)_T = - \frac{\Delta V^\ddagger}{RT} \quad (1)$$

The volume of activation represents the second derivative of the actual physical measurement, concentration as a function of time. Thus it is essential that the data taken be as accurate as possible. Frequently, a relatively small difference in activation volume may have significant meaning. For certain reactions, such as the Diels-Alder reaction, a difference in activation volume of approximately

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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).*

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

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

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

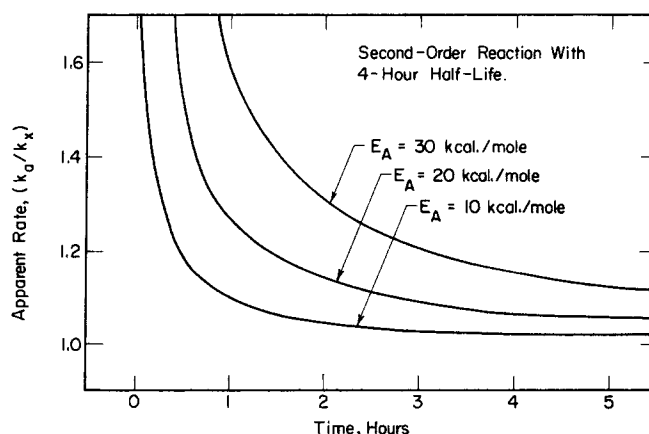


Fig. 1. Effect of an initial temperature rise of 20°C. on the measured rate constant. Temperature half-life = 3.0 min.

* 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)].

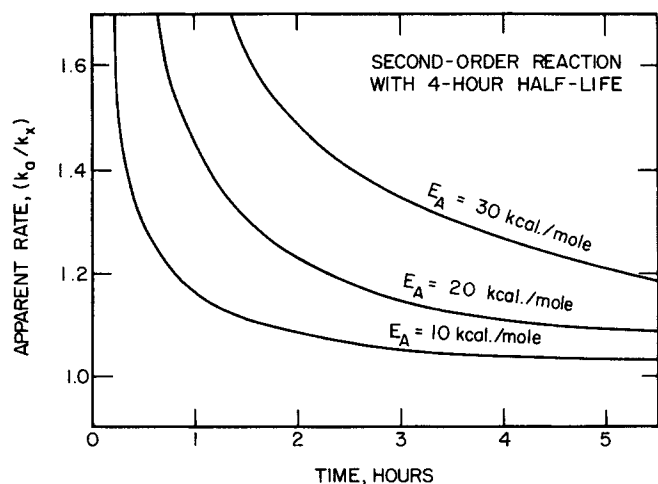


Fig. 2. Effect of an initial temperature rise of 20°C. on the measured rate constant. Temperature half-life = 5.0 min.

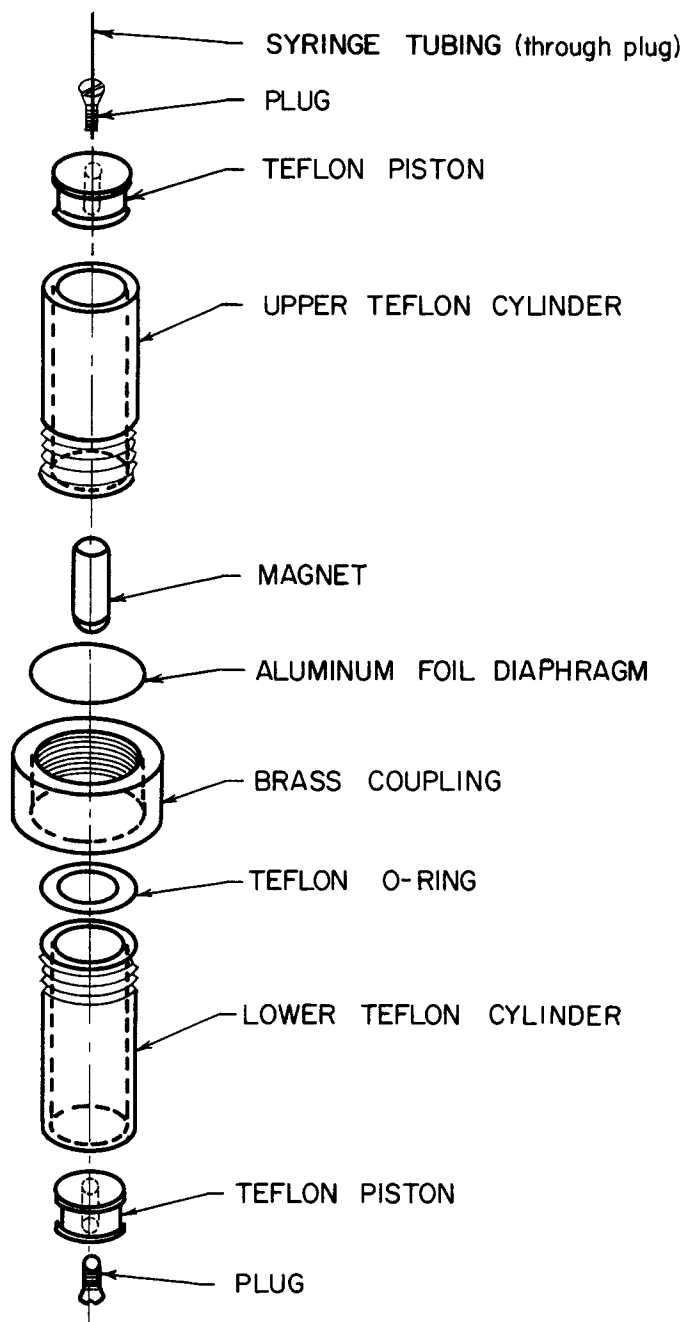


Fig. 3. Expanded drawing of reaction cell.

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.

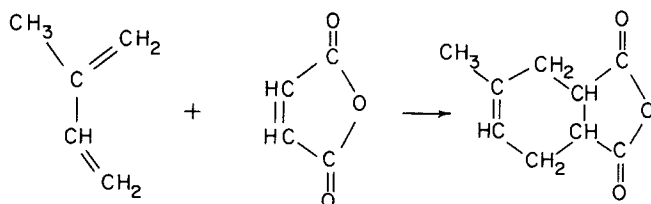
It was found that merely lifting the magnet and dropping it was insufficient to break the foil. Two overlapping coils were wound on the cell, one near the top and the other around the middle. The coils were constructed of No. 32 enameled copper wire at approximately 500 turns/in. By applying a sequence 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

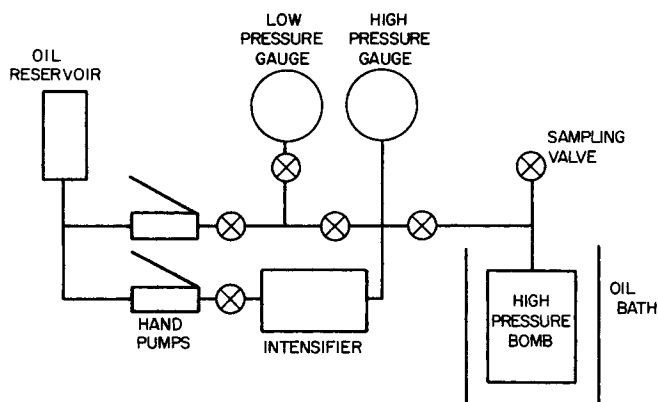


Fig. 4. Schematic diagram of high pressure kinetics apparatus.

piece steel construction, 8 in. in diameter and 17 in. long, with a working space 6 in. long and 1 in. in diameter. Four electrical leads went through the bottom closure, while the lines to the sampling valve and high pressure pump went through the top closure. Rubber o-rings were used for pressure seals, as described by Bridgman (2). Two temperature compensated Heise gauges were used; one had a range of 0 to 15,000 and the other 0 to 100,000 lb./sq.in. The low pressure gauge had been calibrated to ± 15 lb./sq.in. and the high pressure gauge to ± 100 lb./sq.in. The sampling technique was essentially that used by Osborn and Whalley (13), with a Teflon seal separating the pressure transmitting fluid from the reaction mixture being sampled. The sampling valve was a 100,000 lb./sq.in. needle valve with straight-through connections. A $\frac{1}{8}$ -in. hole was drilled through the upper side of the valve just above the valve seat so that the low pressure side of the valve could be flushed with solvent. A plug sealed the hole when samples were being taken. Because the two valve connections are slightly offset, protection is provided if the Teflon pressure seal is extruded. The sampling arrangement is shown in Figure 5.

The temperature of the bomb was controlled by placing it in an oil bath, which was regulated by a continuously operating proportional temperature controller with a thermistor sensor to $\pm 0.02^\circ\text{C}$.

Isoprene was distilled to remove dimer in a Podbielniak 12-in. column packed with nickel helices and stored in a brown glass bottle at 0°C . Purity of the isoprene was better than 99.7%, as shown by gas chromatographic analysis.

Maleic anhydride was distilled at 10 mm./ 82°C . in the same column to remove small amounts of maleic acid. The maleic anhydride thus obtained was stored in a stoppered bottle in a dry box. Purity of the maleic anhydride was tested by washing the sample with two portions of distilled benzene, by decanting the benzene, and by drying and weighing the residue. The maleic acid in the maleic anhydride was less than 0.5% by weight.

Fisher reagent grade ethyl acetate was found to have a trace of an impurity which produced a peak that would interfere with the chromatographic analysis of maleic anhydride. It was therefore distilled in a Podbielniak 36-in. column; the first and last 25% of the distillate were discarded, and the purified ethyl acetate was stored over Linde 4A molecular sieves in brown glass bottles. All distillations were carried out with a 12:1 reflux ratio.

The Diels-Alder adduct, 4-methyl-4-cyclohexene-1,2-dicarboxylic anhydride (MCDA), was recrystallized twice from ethyl ether.

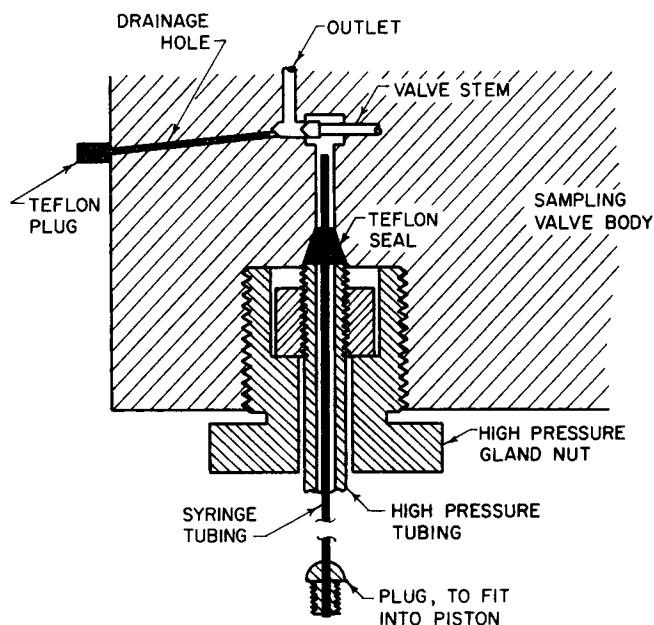


Fig. 5. High pressure sampling apparatus.

Analysis of the samples was made on a Beckman GC-5 gas chromatograph equipped with a hydrogen-flame ionization detector and connected to a Sargent SR recorder with a disk integrator. Two matched $\frac{1}{8}$ -in. O.D. columns, 6 ft. long and packed with 20% DC-11 on a Gas-Pack F support were used in the GC-5. Analyses were based on the measurement of the ratio of product peak area to maleic anhydride peak area. Thus, they were not affected by solvent evaporation or variations in sample size. The chromatograph was calibrated by preparing solutions of various compositions of maleic anhydride and MCDA. Analysis of samples in the concentration range used in the experiments could be duplicated to within $\pm 1.0\%$.

As a check on the mixing and sampling techniques, the rate constant for a reaction run inside the bomb at atmospheric pressure was compared with the rate constant measured in a cell immersed in a temperature bath and shaken manually one hundred times. The two rate constants agreed within 1.0%, which is within the limit of accuracy of the analysis.

RESULTS

Rate constants were measured for the Diels-Alder reaction of isoprene and maleic anhydride in ethyl acetate at 35°C . and pressures up to 6,120 atm. Initial concentra-

TABLE 1. EXPERIMENTAL RATE CONSTANTS
Isoprene-Maleic Anhydride Addition in Ethyl Acetate at 35°C .

Pressure, atm.	Second-order rate constant, mole fraction units, hr. ⁻¹
1	4.41
170	5.59
340	7.12
510	8.95
680	10.98
1,000	15.66
1,361	22.80
2,041	44.34
3,062	112.9
4,083	247.5
5,103	504.9
6,124	1,052.0

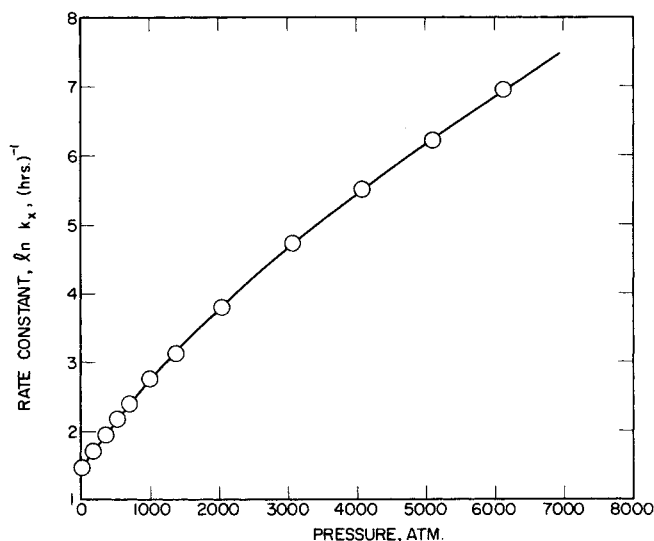


Fig. 6. The effect of pressure on the rate of reaction of isoprene with maleic anhydride in ethyl acetate solution at 35°C.

tions of both reactants were 0.08 to 0.10M. The results, with the rate constant in pressure independent units, are shown in Figure 6, and the exact data are presented in Table 1. To obtain the activation volume at 1 atm. from Equation (1), the points up to 20,000 lb./sq.in. were fit with a quadratic in pressure. The activation volume is -37.4 ± 0.7 cc./g.-mole.

Another method for finding the activation volume at low (zero) pressure, which emphasizes the high pressure points rather than the low pressure ones, was proposed by Benson and Berson (1). They assumed that the Tait equation was applicable to the activated complex. By integrating the expression for activation volume and by approximating part of the integrand with an exponential function, they showed that the activation volume could be calculated from the intercept of a plot of $P^{-1} \ln [k_x(P)/k_x(P=0)]$ vs. $P^{0.523}$. Because of the mathematical approximation in its derivation, such a plot is strictly applicable only at pressures greater than about 2,000 atm. Such a plot for the Diels-Alder reaction of isoprene and maleic anhydride is shown in Figure 7. A good fit is obtained, and ΔV_0^\ddagger calculated from the intercept is -36.5 cc./mole, which agrees well with the value of -37.4 cc./mole calculated from the slope of the $\ln k$ vs. P curve.

By comparison, Walling and Peisach (15) used the classical techniques to measure the rate of dimerization of isoprene and found that up to about 5,000 atm. the $\ln k$ vs. P plot was linear, giving activation volumes of -24.3 cc./mole at 60°C. and -25.6 cc./mole at 75°C. From the same data, using their method, Benson and Berson (1) concluded that the activation volumes were -36.5 cc./mole at 60°C. and -38.4 cc./mole at 75°C.

CONCLUSIONS

A new technique for high pressure kinetics has been reported and has been found to eliminate many of the intrinsic uncertainties in older methods. This technique is capable of yielding the very accurate values for volumes of activation that are needed for determination of the mechanism of reaction or the structure of a transition state as well as for reaction solvent design. By the use of in situ initiation and direct sampling for analysis, the rate of the isoprene-maleic anhydride reaction in ethyl acetate at 35°C. was measured up to 6,120 atm.

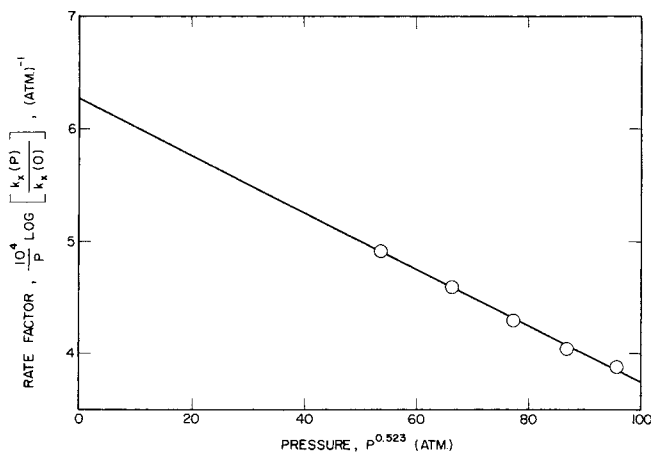


Fig. 7. Data reduction by the method of Benson and Berson: reaction of isoprene and maleic anhydride in ethyl acetate at 35°C.

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NOTATION

- c_1 = constant for temperature decay of apparatus
- c_p = heat capacity at constant pressure
- E_A = activation energy
- k_x = rate constant, mole fraction concentration units
- k_{x0} = rate constant at T_0
- P = pressure
- R = gas constant
- S = entropy
- t = time
- T = temperature
- T_0 = initial (bath) temperature
- T_1 = temperature after compression
- V = volume
- ΔV^\ddagger = volume of activation

LITERATURE CITED

- Benson, S. W., and J. A. Berson, *J. Am. Chem. Soc.*, **84**, 152 (1962).
- Bridgman, P. W., "The Physics of High Pressure," G. Bell, London, England (1949).
- Brower, K. R., *J. Am. Chem. Soc.*, **80**, 2105 (1958).
- Coillet, D. W., and S. D. Hamann, *Trans. Faraday Soc.*, **57**, 2231 (1961).
- Eckert, C. A., *Ind. Eng. Chem.*, **59**, 9, 20 (1967).
- Evans, M. G., and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).
- Gibson, R. O., E. W. Fawcett, and M. W. Perrin, *Proc. Roy. Soc.*, **A150**, 223 (1935).
- Grieger, R. A., M.S. thesis, Univ. Ill., Urbana (1968).
- Griffiss, C. B., and M. C. Henry, *Rubber and Plastics Age*, **46**, 63 (1965).
- Heydtmann, H., A. P. Schmidt, and H. Hartmann, *Berichte der Bunsengesellschaft*, **70**, 444 (1966).
- Koskikallio, J., and E. Whalley, *Trans. Faraday Soc.*, **55**, 809 (1959).
- LeNoble, W. J., *Progr. Phys. Org. Chem.*, **5**, 207 (1967).
- Osborn, A. R., and E. Whalley, *Can. J. Chem.*, **39**, 1094 (1961).
- Sawin, S. P., M.S. thesis, Univ. Ill., Urbana (1968).
- Walling, C., and J. Peisach, *J. Am. Chem. Soc.*, **80**, 5819 (1958).
- Whalley, E., *Advan. Phys. Org. Chem.*, **2**, 93 (1964).

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