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

Fig. 5. High pressure sampling 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 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 ± 0.02°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.
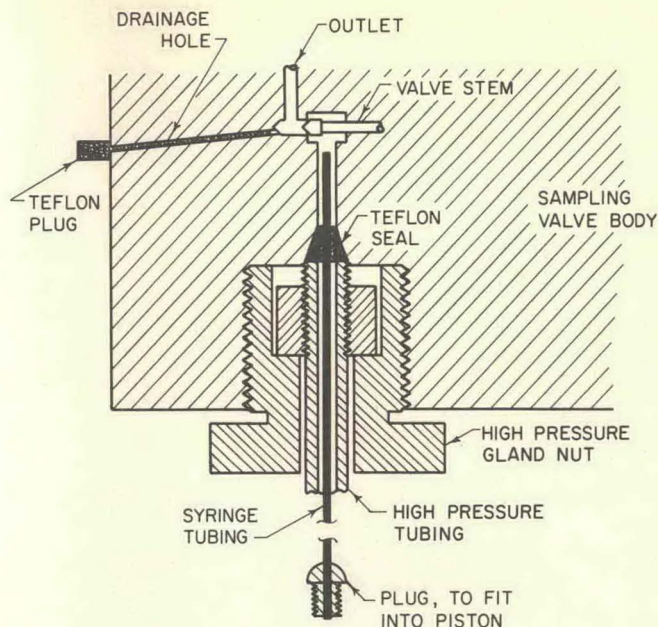
Analysis of the samples was made on a Beckman GC-5 gas chromatograph equipped with a hydrogen-flame ionization detector and connected to a Sargent SR recorder with a disk integrator. Two matched 1/8-in. O.D. columns, 6 ft. long and packed with 20% DC-11 on a Gas-Pack F support were used in the GC-5. 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 ± 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.

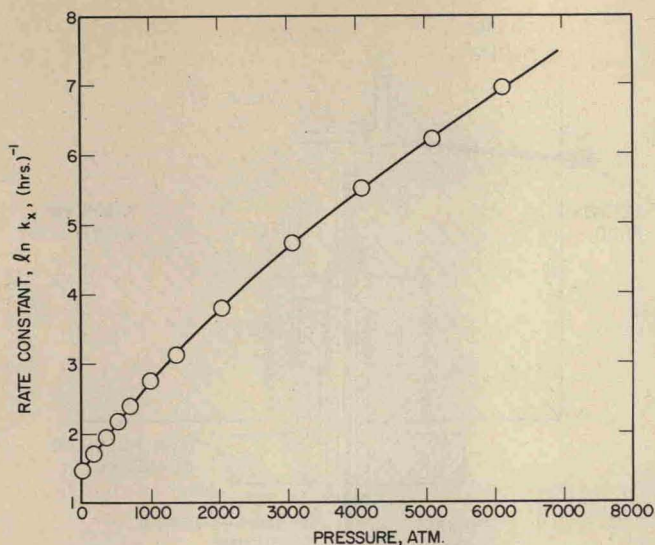| Pressure, atm.	Second-order rate constant, mole fraction units, hr.$^{-1}$
1	4.41
170	5.59
340	7.12
510	8.95
680	10.98
1,000	15.66
1,361	22.80
2,041	44.34
3,062	112.9
4,083	247.5
5,103	504.9
6,124	1,052.0

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

Fig. 7. Data reduction by the method of Benson and Berson: reaction of isoprene and maleic anhydride in ethyl acetate 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 $\Delta V_0^{\neq}$ 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.
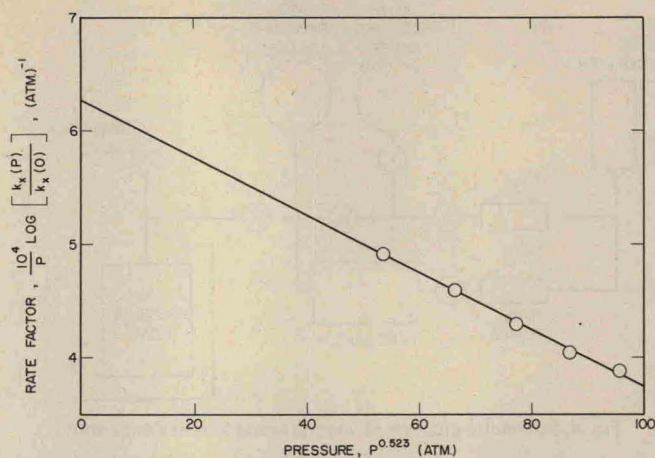
NOTATION

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
$\Delta V^{\neq}$	= volume of activation

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