

diene. Analysis of reaction products was by G.L.C. using an apiezon column at 200°. Rates were followed (after calibrating the area of the product peak with standard (after calibration with known mixtures), but it was also shown both that the disappearance of acrylate corresponded with the appearance of product, and that the ratio of diene peak to acrylate peak remained constant, indicating that no competing reactions were taking place. Second-order rate constants were calculated assuming that the reaction mixture had the same compressibility as bromobenzene,²⁴ and are listed in Table V. Densities of diene, acrylate and product were determined at 80° (using a sealed pycnometer for the diene) as:

2,3-Dimethylbutadiene	d^{80}_4 0.6660
<i>n</i> -Butyl acrylate	.8389
Product	.8984

from which ΔV for the reaction at 80° = -42 cc./mole.

Calculated and measured volumes for a sample of synthetic mixture corresponding to a reaction mixture at 38% conversion were determined as 26.28 and 26.23 ml., respectively, indicating little volume change on mixing of the components and the validity of using bulk molar volumes in place of partial molar volumes in calculating ΔV .

(24) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **66**, 212 (1932).

TABLE V

REACTION OF 2,3-DIMETHYLBUTADIENE WITH *n*-BUTYL ACRYLATE AT 80° UNLESS INDICATED

<i>P</i> , kg./cm. ²	<i>k</i> , l./mole sec. × 10 ⁶	<i>P</i> , kg./cm. ²	<i>k</i> , l./mole sec. × 10 ⁶
1 (70°)	0.347	2000	4.04
1	0.757	3000	8.75
500	1.10	4000	17.2
1000	1.73		

Rearrangement of β -1-hydroxycyclopentadiene was studied in decalin solution, and reaction mixtures were analyzed by infrared spectroscopy using a model 221 Perkin-Elmer recording instrument, calibrated with known mixtures. The peaks of interest are (for the β -alcohol) 768(s) and 756(w) cm.⁻¹ and (for the *anti*-alcohol) 752(s) and 670(w) cm.⁻¹. The product (*anti*-alcohol) is stable under the reaction conditions, while the β -alcohol slowly decomposes. Accordingly, appearance of the product peaks was used in calculation of the rate constants of Table III, although material balances were in general 90-98% complete. Initial concentrations were approximately 3 wt. %, and all reactions gave satisfactory first-order plots over the range studied (1-2 half-lives).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

Organic Reactions under High Pressure. VIII. The Pressure-Dependence of ΔV^* and the Compressibility of Transition States¹

BY CHEVES WALLING AND DENNIS D. TANNER

RECEIVED JULY 18, 1962

The Benson-Berson³ model for the pressure dependence of ΔV^* in which transition states are treated as having compressibility properties similar to ordinary liquids is examined and shown to be plausible only for those systems in which transition states represent volume maxima or minima, since, in others, pressure produces a shift in the transition state along the reaction coordinate. This conclusion is shown to be consistent with the limited amount of data available on the pressure dependence of Cope and Claisen rearrangements and Diels-Alder reactions. Finally, it is suggested that data are best fitted, and ΔV_0^* 's determined, by simple power series of the form $\log k = aP + bP^2 + cP^3 \dots$, rather than by expressions involving explicit transition-state models.

According to transition-state theory, the effect of pressure on the rate of chemical reaction is given by the well-known expression

$$d \ln k/dP = -\Delta V^*/RT \quad (1)$$

where ΔV^* , the "activation volume," represents the difference in volume between reactants and transition state.² As several workers have shown, values of ΔV^* can in turn provide useful information in reaction mechanism studies by indicating the molar volumes of the transition states involved. Unfortunately, the problem is complicated by the fact that ΔV^* is not a pressure-independent quantity, and, since the value at atmospheric pressure is usually that desired, it must be estimated from a curved plot of $\ln k$ vs. P . On the other hand, if an adequate theory of the pressure dependence of ΔV^* were available, this dependence might be used to gain additional information about transition states. These considerations have recently been pointed out by Benson and Berson³ in a very interesting and significant paper. Here we will attempt to develop these ideas further and show how our interpretation differs from theirs. Our discussion will be restricted to essentially non-ionic processes, *i.e.*, radical reactions, Diels-Alder type processes and "four-center" reactions such as Cope rearrangements which show no great dependence on solvent polarity or ionizing power, since the interpretation of pressure effects on ionic reactions appears to be even more complex.^{3,4}

The Benson and Berson Model for Transition State Compressibility.—Benson and Berson³ have proposed

(1) Support of this work by a grant from the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

(2) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).

(3) S. W. Benson and J. A. Berson, *J. Am. Chem. Soc.*, **84**, 152 (1962).

(4) S. D. Hamann, "Physico Chemical Effects of Pressure," Academic Press, Inc., New York, N. Y., 1957.

a model for the variation of ΔV^* with pressure which assumes that both reactant and transition state in a non-ionic reaction may be treated as normal molecules with equations of state following the Tait equation

$$dV/dP = -J/(K + P) \quad (2)$$

or, in integrated form⁵

$$(V_0 - V_p)/V_0 = C \log(1 + P/B) \quad (3)$$

where V_0 represents molar volume at essentially zero pressure (1 atmosphere) and the parameters in the two forms are related as

$$J = V_0 C/2.303, K = B$$

If an expression similar to 2 is written for a transition state

$$dV^*/dP = -J^*/(K^* + P) \quad (4)$$

and 1, 2 and 4 combined, we obtain

$$RT d^2 \ln k/dP^2 = J^*/(K^* + P) - J/(K + P) \quad (5)$$

Equation 5 now represents a concise expression for the pressure dependence of k , suitable for machine computation. Its completely integrated form has been given by Benson and Berson, but is too complex to reproduce here. For organic liquids in general, C is almost constant, having values of 0.205-0.225, while B ($=J$) varies from 300-1200 kg./cm.². The initial compressibilities of liquids are given by J/K , and vary considerably. At high pressures, $P \gg K$, all liquids show similar compressibilities and 2 is approximated by

$$dV = J \ln P \quad (6)$$

The parameter B varies in a systematic and predictable manner for different liquids, increasing with molecular weight and density, and decreasing with increasing temperature. It is larger for polar molecules (particularly those held together by hydrogen bonding)

(5) Equation 3 is misstated in ref. 3 and is correct as given here.

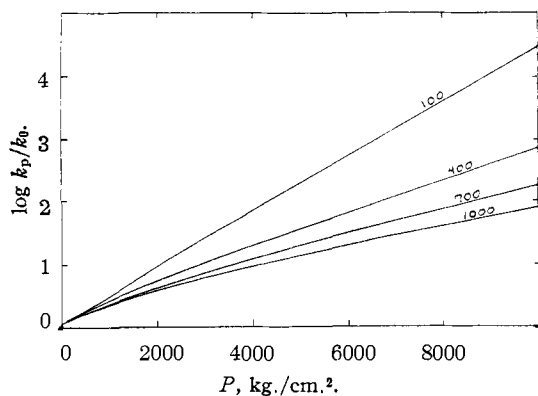


Fig. 1.—Calculated variation of k_p with pressure for model reaction at 60° from eq. 5: V_0 , 106 cc./mole; B , 330 kg./cm.²; C , 0.226; V_0^* , 80 cc./mole; B^* , as indicated; C^* , 0.226.

than for hydrocarbons of the same molecular weight. These variations are also consistent with a picture of liquid compressibility in the region with which we are concerned (1–10,000 kg./cm.²) in which volume changes are primarily the result of van der Waals compression between molecules and the squeezing out of liquid holes, rather than any changes on the length of internal covalent bonds.⁶

An idea of the types of $\log k$ vs. P plots which are predicted by eq. 5 is given by Fig. 1. Here values of B and V have been chosen as plausible for a C₃-hydrocarbon, ΔV_0^* has been taken as -26 cc./mole and B^* varied systematically. It may be seen that, although all curves have the same initial slope, for $B^* > B$ (a relatively incompressible transition state) curves are strongly concave downward, but become straighter as B^* decreases. In fact, for small enough values of B^* , an inflection actually occurs, and the initial part of the curve is concave upward.

While plots such as Fig. 1 are relatively simple to calculate for any single set of parameters, fitting of a solution of 5 to a set of experimental points is a much more formidable operation.⁷ To simplify the procedure, Benson and Berson have suggested that the completely integrated form of 5 is well approximated between 3000 and 10,000 kg./cm.² by a simple expression of the form

$$(\log k_p/k_0)/P = A + BP^{0.523} \quad (7)$$

where

$$A = -\Delta V_0^* (1 - 0.008C)/2.303RT$$

Accordingly, by plotting the left-hand side of 7 vs. $P^{0.523}$ and extrapolating to $P = 0$, ΔV_0^* can be obtained accurately from experimental data at higher pressures. In Fig. 2, such plots are illustrated for the curves of Fig. 1. The calculated extrapolation point is also indicated, and it is plain that any actual extrapolation would give results quite dependent of B^* .

Factors Determining Transition State Compressibility.—In considering the plausibility of the Benson-Berson treatment, or any model treating the pressure dependence of ΔV^* , it is necessary to consider the volume changes occurring as a system passes from reactants to products. We believe that three types of behavior may be distinguished and identified with different types of simple reaction.

Type I: Transition State a Volume Minimum.—Such behavior is illustrated by the upper curves of Fig. 3, and would be predicted for a radical (or other

(6) Although the Tait equation is an empirical expression, a derivation from theory, based on this general picture, has recently been suggested, R. Ginelli, *J. Chem. Phys.*, **34**, 1249 (1961).

(7) Computations used in this paper were carried out by J. Muldoon of our Department of Chemical Engineering, using a digital computer.

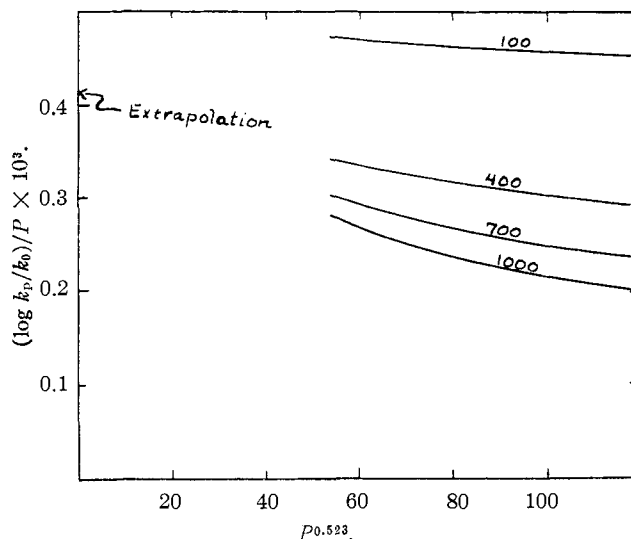


Fig. 2.—Determination of ΔV_0^* by Benson-Berson extrapolation. Parameters have the same values as in Fig. 1.

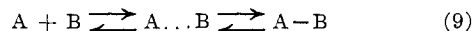
non-ionic) displacement



Here ΔV^* will be negative, no shift of the transition state along the reaction coordinate with pressure will occur, and the hypothesis that the compressibility of the transition state will approximate that of a stable molecule of the same size and composition seems quite plausible. "Four-center" rearrangements such as Claisen and Cope rearrangements which are pressure accelerated⁸ and are thought to involve cyclic transition states with simultaneous bond breaking and bond forming would also fall in this class.

Type II: Transition State a Volume Maximum.—This type, illustrated by the middle curves of Fig. 3, would show a positive value of ΔV^* , and again would show no shift of transition state with pressure. This would seem to be a relatively rare class, but might be represented by purely thermal *cis-trans* isomerizations, or sterically hindered racemizations.⁹

Type III: Monotonous Volume Change Along Reaction Coordinate.—In this class (bottom curves of Fig. 3) the transition state is not a volume extremum, and such behavior would be expected of a whole group of reactions of the general type



Diels-Alder type reactions would belong to this class (regardless of the one- or two-step nature of the mechanism) as would radical couplings and disproportionations. Radical additions to double bonds probably also do not show volume minima along the reaction coordinate, while radical dissociations would be type III reactions running from right to left. Here the assumption that transition state compressibility is similar to that of a normal molecule is much more dubious since, as shown below, pressure actually leads to a displacement of the transition state position along the reaction coordinate.

Ignoring for the time being any normal compression of reactant molecules or transition states, the effect of pressure on a reaction rate may be visualized in terms of the curves of Fig. 3 as follows. If ΔF_x is thought of as the partial molar free energy of the reactants at some point x on the reaction coordinate minus that of the reactants, and ΔV_x the corresponding differ-

(8) C. Walling and M. Naiman, *J. Am. Chem. Soc.*, **84**, 2628 (1962).

(9) A positive value of ΔV^* for the racemization of dinitrodiphenic acid has been reported by C. C. McCune, F. W. Cagle, Jr., and S. S. Kistler, *J. Phys. Chem.*, **64**, 1773 (1960).

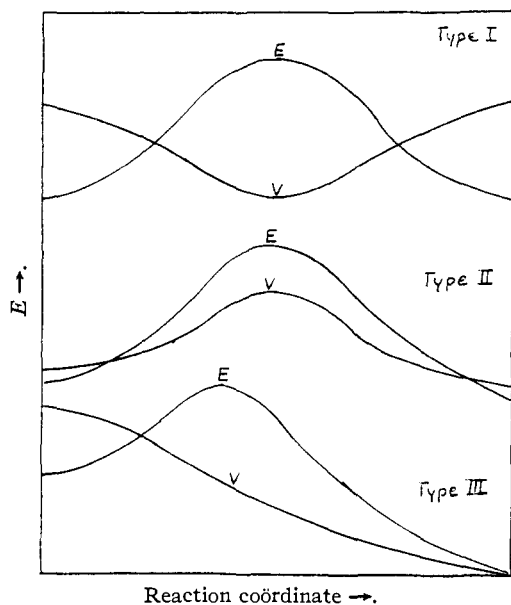


Fig. 3.—Relation between energy and volume along reaction coordinate for different reaction types.

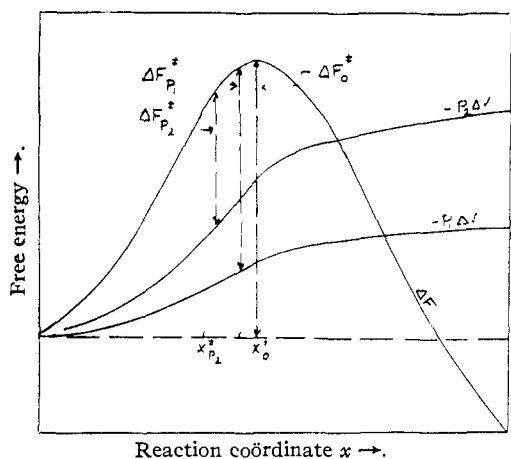


Fig. 4.—Illustration of displacement of transition state along reaction coordinate by pressure for type III reactions.

ence in partial molar volumes, the application of pressure will change this energy difference

$$\Delta F_{p,x} = \Delta F_x + P\Delta V_x \quad (10)$$

This relation is shown more clearly for a type III reaction in Fig. 4, where ΔF_p is clearly the difference between the two curves. The maximum in ΔF , ΔF_0^* , is the transition state at zero pressure, but, since the functions $-P\Delta V$ have a positive slope at this point, under pressure this maximum will be shifted to the left to a point defined by

$$d(\Delta F)/dx = -Pd\Delta V/dx \quad (11)$$

and indicated by the vertical arrows. Further, since at any one pressure $d(\Delta F)/dx < -Pd\Delta V/dx$, everywhere between x^* and x_p^* , the resulting value of ΔF_p^* will be greater than $\Delta F_{p,x}^*$, the free energy difference if no shift had occurred. Although the magnitude of this change can only be calculated if the functional relation between ΔF and ΔV is known, it is plain that it will contribute a term to transition state compressibility as defined by eq. 1 which is not accommodated by any treatment of the transition state as a normal molecule. Accordingly, we conclude that any theoretical treatment of the pressure dependence of ΔV^* for this class of reactions will be particularly difficult.¹⁰

(10) In this regard, any displacement reaction in which the structure A...C represents a metastable molecule (*i.e.*, a slight valley in the energy contour) would fall into class III as well.

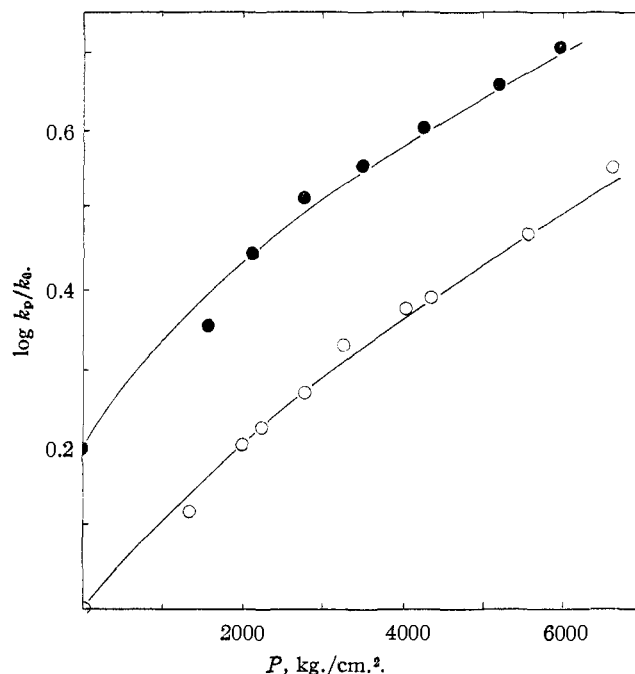


Fig. 5.—Tait equation treatment of type I reactions: open circles, Cope rearrangement of I: V_0 , 300 cc./mole; B , 1500 kg./cm.²; C , 0.216; V_0^* , 290 cc./mole; B^* , 1800 kg./cm.²; C^* , 0.216. Closed circles, Claisen rearrangement of allyl phenyl ether (all points displaced upward 0.2 log unit): V_0 , 155 cc./mole; B , 500 kg./cm.²; C , 0.216; V_0^* , 140 cc./mole; B^* , 900 kg./cm.²; C^* , 0.216.

Treatment of Experimental Data.—Relatively few data collected over an adequate pressure range on suitable molecules are available for testing theories of transition state compressibility, and our discussion here will be restricted to five systems involving what should be type I and type III reactions. As examples of type I, the Claisen rearrangement of allyl phenyl ether and the Cope rearrangement of ethyl (1-ethylpropenyl)-allylcynoacetate (I) have been studied in this Laboratory.⁸ Each reaction was investigated in several solvents, with the conclusion that ΔV^* was negative in each case and essentially solvent independent. Using data in that solvent which gave the smallest scatter of experimental points, we have attempted to determine the best fit to eq. 5 by selecting the values of B , C and V_0 indicated, setting $C^* = C$, and systematically varying B^* and V_0^* . Parameters chosen and the resulting "best" curves are shown in Fig. 5. Fits to the data seem reasonable, and in each case B^* is slightly larger than B , as might be expected for cyclic transition states less compressible than the open-chain reactants. Values of ΔV_0^* , -15 cc./mole for the Claisen rearrangement and -10 cc./mole for the Cope rearrangement, also are not out of line.

Data on Type III reactions are available for three Diels-Alder reactions, the dimerization of isoprene¹¹ and of cyclopentadiene,¹² and the reaction of butyl acrylate with 2,3-dimethylbutadiene.¹² Benson and Berson have applied their Tait equation treatment (in its approximate form) to the isoprene data, and shown that plots of $(\log k_p/k_0)/P$ vs. $P^{0.523}$ are sharply curved with considerable scatter of points at lower pressures. Accordingly, they elected to use only points above 5000 kg./cm.² for the extrapolation to zero pressure, and obtained $\Delta V^* = -36.5$ cc./mole at 60°, compared with -24.3 cc./mole from simple plotting of the original data. Their parameters yield a calculated plot of log

(11) C. Walling and J. Peisach, *J. Am. Chem. Soc.*, **80**, 5819 (1958).

(12) C. Walling and H. J. Schugar, *ibid.*, **85**, 607 (1963).

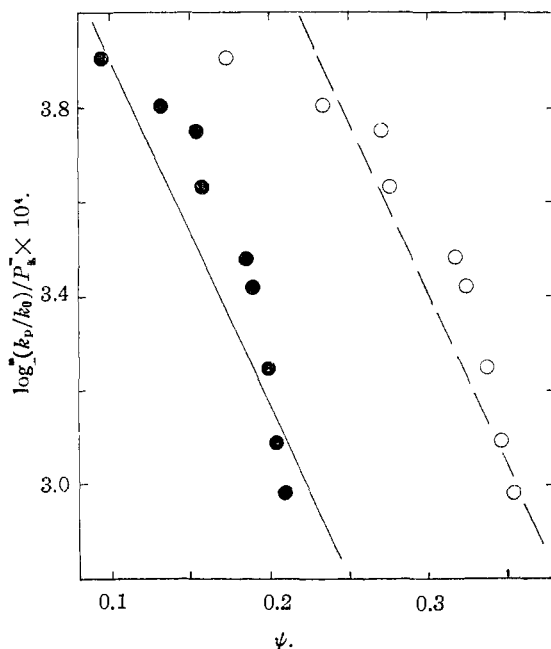


Fig. 6.—Tait equation treatment of isoprene dimerization at 60°: solid line: ΔV_0^* , -30 cc./mole; B , 360; C , 0.216; B^* , 300; C^* , 0.216. Dashed line, Benson-Berson parameters: ΔV_0^* , -36.5 cc./mole; B , 300; B^* , 525; C , 0.216; C^* , 0.216.

k_p/k_0 vs. P which lies slightly above all experimental points for pressures below 4000 kg./cm.². Systematic variation of transition state parameters indicate that better fits in the low pressure region can be obtained by choosing smaller values of B^* and less negative values of ΔV_0^* , but that no choice fits the entire range. $\log k$ vs. P plots do not show these changes very well, and Benson and Berson have suggested that a more sensitive test is to plot $\log(k_p/k_0)/P$ vs. Ψ (a function of P , V_0 's and the Tait parameters). If the integrated form of the Tait equation is obeyed exactly, the result will be a linear plot with a predicted slope and intercept. Such plots are shown in Fig. 6, using both the Benson-Berson parameters, and a set which gives the best fit that we have been able to obtain over the entire range on a $\log k$ vs. P plot. What this treatment appears to us to show is that neither choice of parameters provides more than a rough fit of the data to the exact Tait equation treatment of transition state compressibility; the fits are comparable at high pressures, but our choice of parameters accommodates better the data at lower pressures (upper points in the figure). On the other hand, the value of B^* which must be used is implausibly small for a "normal" C₁₀-hydrocarbon, and indicates an abnormal compressibility for the transition state. Essentially the same results (not shown) are obtained with experimental data at 75°.

Similar conclusions result when 5 is applied to the other available experimental results on Diels-Alder reactions. "Best fits" on $\log k$ vs. P plots and the corresponding parameters required are shown in Fig. 7. In each case, while reasonable fits are obtained, much lower values of B^* are required than would be expected for normal molecules.

Conclusions.—On the basis of the considerations we have developed concerning volume-energy relations along reaction coordinates and our examination of

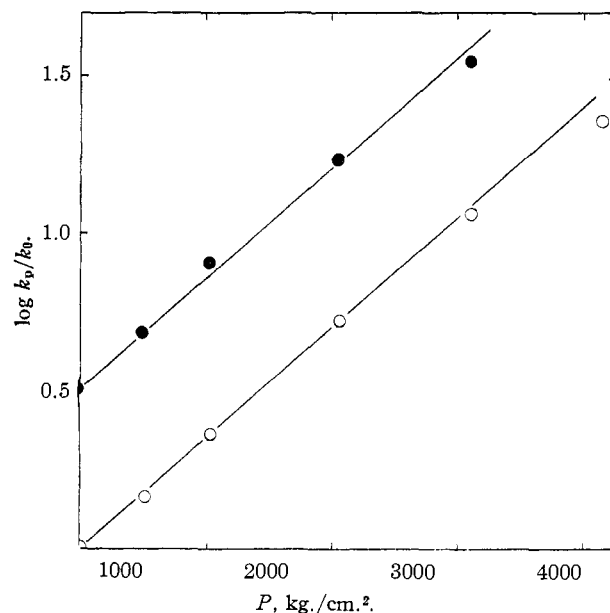


Fig. 7.—Tait equation treatment of other Diels-Alder reactions: open circles, 2,3-dimethylbutadiene-butyl acrylate (80°): ΔV_0^* , -22.6 cc./mole; B , 2000 kg./cm.²; B^* , 1600 kg./cm.²; C , 0.216; C^* , 0.216. Closed circles, cyclopentadiene dimerization (30°) (all points displaced upward 0.5 log unit): ΔV_0^* , -18.9 cc./mole; B , 599 kg./cm.²; B^* , 480 kg./cm.²; C , 0.216; C^* , 0.216.

available experimental data, we conclude that any theory of the pressure dependence of ΔV^* which treats transition states as having the compressibility properties of ordinary molecules is at best restricted to the small group of non-ionic reactions in which transition states represent volume maxima or minima. Even here, confirmation is restricted to only two systems, and additional data are certainly necessary.¹³

With this said, however, we are still left with the problem of determining ΔV_0^* 's from experimental data, chiefly gathered at relatively high pressures. For reactions giving fairly linear $\log k$ vs. P plots including the point at atmospheric pressure, e.g., most of the Diels-Alder data, straightforward graphical treatment is probably as satisfactory as any. For the majority of reactions which show marked curvature at low pressures, the importance of good measurements in the interval up to 2000 kg./cm.² is critical and has not been generally appreciated. A power series treatment of the resulting data would then seem the simplest and most conventional approach, particularly since for the expression

$$-RT \ln k_0/k_p = aP + bP^2 + cP^3 + \dots \quad (12)$$

$a = \Delta V_0^*$, b is the coefficient of initial compressibility of ΔV^* , and c, \dots represents higher pressure corrections.

When 12 is applied to the Claisen and Cope data of Fig. 5, using terms through cP^3 , fits are obtained quite comparable to those resulting from the much more tedious use of 5, and essentially the same values of ΔV_0^* result.

(13) Benson and Berson³ have also applied their approximate treatment to data on the decomposition of azobisisobutyronitrile, followed by iodine consumption. However, this is a type III reaction complicated, as they note, by a cage effect. Accordingly, the poor fit they report probably has little significance.