PRESSURE AND RATE PROCESSES[1]

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When kT times the natural logarithm of the specific reaction rate constant is plotted as ordinate against the pressure as abscissa the slope of the line gives the total difference in volume between the reactant molecules and the activated complex. Here k is the Boltzmann constant and T is the absolute temperature. More precise rules are formulated for predicting the volume increments, for various types of reaction, than those given in earlier papers by Evans and Polanyi or in previous papers from this laboratory. Simple theoretical calculations of the effect of pressure are compared with experimental values for the available unimolecular and bimolecular reactions as well as for viscous flow. The agreement is satisfactory, and the study of pressure effects is seen to lead to the same sort of insight into reaction mechanism that is provided by a study of the temperature effect.

If one knows the volume change in going from the normal to the activated state, the effect of pressure on reaction rates can be predicted in the same way as for equilibria. Formulae for this volume change which depend only on the structure of the reactants are given for unimolecular and bimolecular reactions and for viscous flow and the predicted results are seen to agree well with experiment. When the effect of pressure and temperature on the reaction rates and on the properties of the reactants are known from experiment, it is possible to calculate all the thermodynamic properties of the activated complex. Such calculated results are given for a variety of reactions.

The theory of absolute reaction rates reduces the expression for the rate constant to three factors,—a frequency, an equilibrium constant, and a transmission coefficient

$$k' = \frac{kT}{h} K^{\ddagger} \tag{1}$$

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where $K^{\ddagger}$ measures the concentration of activated complex in equilibrium with unit concentration of reactants. In effect, the value of the rate constant gives the value of $\Delta F^{\ddagger}$, the standard free-energy change for the formation of the activated complex. Measurements of k' through both a temperature and a pressure range, together with data on the compressibilities of the reacting materials, give knowledge of the effect of temperature, of pressure, and of volume on $\Delta F^{\ddagger}$, and lead directly to six partial derivatives (and implicitly to many others), so that, if the thermodynamic properties of the ground state of the reacting system are known, all the thermodynamic properties of the activated complex may be obtained. The effect of pressure on reaction rates, from the thermodynamic point of view, has been discussed by Evans and Polanyi (7) and by Stearn and Eyring (17).

In this paper are presented the results of a study of rate processes which have been investigated at high pressures. Such processes include viscous flow. The viscosity and compressibility data are those of Bridgman (and are to be found, for the most part, in reference 1). Other thermodynamic data were obtained from *International Critical Tables* and the Landolt–Börnstein *Tabellen*.

In table 1 are given the results of a somewhat detailed study of five processes: the viscous flow of three typical substances—the metal mercury, the hydrogen-bonded liquid glycerol, and ether—the bimolecular reaction between pyridine and ethyl iodide (11), and the monomolecular decomposition of phenylbenzylmethylallylammonium bromide (20).

For fluidities we use a modified form of the equation developed by Eyring (8).

$$\varphi = \frac{\lambda^2 \lambda_2 \lambda_3}{\lambda_1 h} e^{-\frac{\Delta F^{\ddagger}}{RT}} \tag{2}$$

where we take

$$\frac{\lambda^2 \lambda_2 \lambda_3}{\lambda_1 h} = \frac{V}{N}$$

V being the molal volume and N Avogadro's number.

Thus we have for fluidities

$$\Delta F^{\ddagger} = RT \ln \frac{V}{\varphi N h} \tag{3}$$

and for chemical reactions

$$\Delta F^{\ddagger} = RT \ln \frac{kT}{k'h} \tag{4}$$

we use the Lewis and Randall conventions. For values of k', in place of the unimolecular constant frequently reported for "first-order" bimolecular reactions such as hydrolyses, we use the bimolecular constant. The following are the particular relationships used in calculating the values of the various thermodynamic quantities in table 1:

$$\left(\frac{\partial \Delta F^{\ddagger}}{\partial P}\right)_T = \Delta V^{\ddagger} \tag{5}$$

$$\left(\frac{\partial \Delta F^{\ddagger}}{\partial T}\right)_P = -\Delta S^{\ddagger} \tag{6}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = \alpha V \tag{7}$$

$$\left(\frac{\partial \Delta F^{\ddagger}}{\partial V}\right)_T = \frac{1}{\beta_n} - \frac{1}{\beta^{\ddagger}} \tag{8}$$

$$\left(\frac{\partial \Delta F^{\ddagger}}{\partial V}\right)_P = \frac{S_n}{\alpha_n V_n} - \frac{S^{\ddagger}}{\alpha^{\ddagger} V^{\ddagger}} \tag{9}$$

$$\left(\frac{\partial \Delta F^{\ddagger}}{\partial T}\right)_P = \Delta C_P^{\ddagger} + P(\alpha_n V_n - \alpha^{\ddagger} V^{\ddagger}) \tag{10}$$

For calculating the properties of the activated complex in the bimolecular reaction between pyridine and ethyl iodide we have made the following approximations: (1) The partial molal volumes of the two reactants in solution are the same as in the pure liquid state, as are also their coefficients of compressibility and of thermal expansion. (2) Since the molal volumes of pyridine and of ethyl iodide are nearly equal, we use average values of α and β for the normal state. (Data for pyridine are lacking and we assume it to behave under pressure as does phenyl chloride.)

In table 2 we give a more limited number of thermodynamic quantities for a larger number of reactions. For monomolecular reactions, including the process of viscous flow, there is an increase in volume on activation, so that increased pressure decreases the rate of the process. Fawcett and Gibson (9) have studied in a qualitative way the effect of pressures up to 3000 atmospheres on the rates of about fifty organic reactions. In all cases where the reaction proceeded at 1 atmosphere, the rate was increased by increased pressure. These reactions were all at least bimolecular. For the bimolecular reactions cited in tables 1 and 2 (as well as table 3), formation of the activated complex involves a decrease in volume.

For ordinary chemical reactions the volume change on activation at low pressures can be quite accurately calculated, when electrostriction changes

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TABLE 1

Results of a detailed study of five processes

P	$\varphi_{30}°$	V	$\Delta F^{\ddagger}$	$\Delta V^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta E^{\ddagger}$	$\alpha_n \times 10^4$	$\alpha^{\ddagger} \times 10^4$	$\beta_n \times 10^5$	$\beta^{\ddagger} \times 10^5$	$\Delta C_P^{\ddagger}$	$\Delta H^{\ddagger}$
Viscous flow of glycerol												
1	0.263	73.46	6,718	15.0	19.6	12,720	5.3	4.5	2.4	2.0	0	12,720
500	0.193	72.64	6,896	14.2	19.9	12,755	4.7	4.0	2.2	1.82	0.24	12,926
1,000	0.145	71.90	7,061	13.4	20.1	12,826	4.4	3.7	1.96	1.64	0.71	13,151
2,000	0.084	70.61	7,380	12.7	21.1	13,158	4.15	3.5	1.63	1.39	1.29	13,773
4,000	0.0305	68.58	7,970	11.8	21.4	13,310	3.7	3.1	1.34	1.16	4.57	14,454
6,000	0.0119	66.93	8,523	11.2	25.7	14,682	3.3	2.75	1.14	0.99	10.09	16,310
8,000	0.00478	65.50	9,059	11.0	28.3	15,501	3.6	3.0	1.00	0.86	10.04	17,633
10,000	0.00194	64.26	9,590	10.9	30.6	16,219	3.9	3.1	0.88	0.75	13.3	18,860
Viscous flow of ether												
1	471.6	105.5	2,427	20.	−5.0	912	16.9	14.	16.	14.1	0	912
500	304.	98.34	2,650	14.7	−4.55	1,094	11.0	9.5	10.8	9.6	0.3	1,271
1,000	223.6	94.19	2,782	10.8	−4.35	1,204	8.55	7.53	6.8	6.1	0.4	1,464
2,000	144.	89.08	3,039	8.8	−4.05	1,384	5.73	5.1	4.8	4.4	0.1	1,812
4,000	76.1	83.01	3,381	6.8	−4.7	1,486	5.0	4.6	2.8	2.5	0.3	2,148
6,000	42.7	79.31	3,700	6.2	−3.9	1,612	4.42	4.1	1.94	1.8	1.7	2,518
8,000	25.85	76.57	3,984	5.7	−3.6	1,786	3.73	3.42	1.68	1.57	0.6	2,893
10,000	16.0	74.49	4,254	5.5	−3.6	1,830	3.44	3.20	1.48	1.38	3.3	3,163
12,000	10.08	72.64	4,517	5.3	−2.33	2,270	3.26	3.04	1.3	1.21	7.1	3,811
Viscous flow of mercury												
1	65.96	14.84	2,430	0.50	−6.22	545	1.78	2.0	0.40	0.38	0	545
2,000	63.09	14.72	2,454	0.48	−6.24	540	1.67	1.93	0.37	0.36	−0.27	563
4,000	60.13	14.61	2,476	0.50	−6.31	515	1.60	1.86	0.35	0.337	−0.48	564
6,000	57.40	14.51	2,503	0.51	−6.27	529	1.54	1.76	0.325	0.316	−0.68	603
8,000	54.88	14.39	2,526	0.50	−6.34	508	(1.5)	1.4	0.30	0.29		605
10,000	52.30	14.34	2,551	0.52	−6.42	480	(1.76)	1.68	0.27	0.25	−1.4	606
12,000	49.83	14.26	2,576	0.52	−6.31	513	(1.43)	1.61	0.24	0.23	−1.63	664

Pyridine and ethyl iodide in acetone solution, $t_1 = 30°C$. (reference 11)

P	$k' \times 10^4$	V	$\Delta F^\ddagger$	$\Delta V^\ddagger$	$\Delta S^\ddagger$	$\Delta E^\ddagger$	$\alpha_n \times 10^4$	$\alpha^\ddagger \times 10^4$	$\beta_n \times 10^5$	$\beta^\ddagger \times 10^5$	$\Delta C_P^\ddagger$	$\Delta H^\ddagger$
atm.												
1	0.143	162.6	24,440	−20.	−34.4	14,030	10.4	11.6	7.2	8.0	0	14,030
3,000	1.033	140.6	23,250	−12.7	−28.4	15,568	5.6	4.9	2.5	2.7	7	14,645
5,000	2.13	133.9	22,816	−8.55	−24.4	16,447	4.3	3.5	1.9	2.0	8.6	15,423
8,500	6.5	126.9	22,145	−7.4	−21.5	17,113	4.3	3.5	1.2	1.3	4.7	15,630

Decomposition of phenylbenzylallylmethylammonium bromide in chloroform (20)

P	$k'_{25°} \times 10^5$	$k'_{45°} \times 10^4$	$\Delta F^\ddagger_{25°}$	$\Delta F^\ddagger_{45°}$	$\Delta V^\ddagger_{25°}$	$\Delta V^\ddagger_{45°}$	$\Delta S^\ddagger$	$\Delta E^\ddagger_{25°}$	$\Delta E^\ddagger_{45°}$	$\Delta A^\ddagger_{25°}$	$\Delta A^\ddagger_{45°}$	$\Delta C_P^\ddagger$	$\Delta H^\ddagger$
atm.													
1	1.0	1.98	24,237	24,018	3.4	2.25	11.	27,515	27,515	24,237	24,018	0	27,515
3,000	0.66	1.53	24,483	24,181			15.1	28,736	28,819	24,236	24,017	4.15	28,983

TABLE 2

Thermodynamic quantities for certain reactions

REACTION	P	$\Delta F_{t_1}^{\ddagger}$	$\Delta F_{t_2}^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta V_{t_1}^{\ddagger}$	$\Delta V_{t_2}^{\ddagger}$
	atm.						
Viscous flow: $t_1 = 30°C.; t_2 = 75°C.$							
H₂O	1	2,166	1,988	3,378	4.0	0.16	0.83
	4,000	2,272	2,116	3,332	3.5		
	10,000	2,503	2,399	3,200	2.3	1.4	1.3
CH₃OH	1	2,394	2,442	2,061	−1.1	8.3	9.2
	4,000	2,930	2,988	2,536	−1.3		
	12,000	3,585	3,609	3,434	−0.5	3.2	3.0
C₂H₅OH	1	3,013	2,948	3,437	1.4	9.5	11.5
	4,000	3,753	3,802	3,420	−1.1		
	12,000	4,747	4,710	4,989	0.8	4.9	4.3
n-C₃H₇OH	1	3,504	3,419	4,080	1.9	15.3	17.4
	4,000	4,565	4,504	4,958	1.3		
	12,000	5,993	5,791	7,357	4.5	6.8	6.0
i-C₃H₇OH	1	3,512	3,281	5,057	5.1	19.6	22.0
	4,000	4,770	4,605	5,891	3.7		
	12,000	6,542	6,108	9,451	9.6	9.3	7.3
n-C₄H₉OH	1	3,766	3,632	4,675	3.0	18.4	16.5
	4,000	4,965	4,723	6,601	5.4		
	6,000	5,435	5,297	6,374	3.1	9.7	11.8
i-C₄H₉OH	1	3,970	3,650	5,738	6.0	21.7	25.1
	4,000	5,477	5,167	7,568	6.9		
	12,000	7,756	7,244	11,210	11.4	11.6	12.4
n-Pentane	1	2,514	2,642	1,666	−2.8	14.8	18.2
	4,000	3,531	3,797	1,743	−5.9		
	10,000	4,529	4,730	3,165	−4.5	7.0	6.0
Isopentane	1	2,458	2,593	1,549	−3.0	19.2	22.4
	4,000	3,544	3,799	1,817	−5.7		
	10,000	4,578	4,777	3,245	−4.4	7.0	6.0
n-Hexane	1	2,764	2,910	1,794	−2.2	16.0	20.3
	4,000	3,903	4,154	2,206	−5.6		
	8,000	4,684	4,890	3,290	−4.6	7.7	7.4
n-Octane	1	3,190	3,399	1,796	−4.6	19.9	21.9
	4,000	4,583	4,756	3,432	−3.8		
	6,000	5,111	5,231	4,293	−2.7	4.7	9.8

TABLE 2—*Continued*

REACTION	P	$\Delta F^{\ddagger}_{t_1}$	$\Delta F^{\ddagger}_{t_2}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta V^{\ddagger}_{t_1}$	$\Delta V^{\ddagger}_{t_2}$
	atm.						
Ethyl bromide............	1	2,559	2,688	1,832	−2.4	11.4	14.6
	4,000	3,315	3,566	1,618	−5.6		
	12,000	4,302	4,509	2,908	−4.6	4.8	4.4
Ethyl iodide..............	1	2,833	3,031	1,500	−4.4	11.0	12.3
	4,000	3,631	3,882	1,934	−5.6		
	12,000	4,793	4,959	3,672	−3.7	5.9	5.3
n-Butyl bromide..........	1	3,006	3,221	1,552	−4.8	14.3	15.5
	4,000	4,030	4,241	2,606	−4.7		
	12,000	5,620	5,622	5,620	0	8.4	7.0
Acetone.................	1	2,397	2,632	821	−5.2	14.7	12.5
	4,000	3,116	3,339	1,601	−5.0		
	10,000	3,818	3,980	2,727	−3.6	4.6	4.0
Carbon disulfide..........	1	2,403	2,602	1,070	−4.4	8.3	9.7
	4,000	3,000	3,241	1,364	−5.4		
	12,000	3,865	4,061	2,532	−4.4	4.8	4.1
Phenyl chloride...........	1	3,065	3,254	1,792	−4.2	13.8	14.0
	1,000	3,381	3,587	1,987	−4.6		
	2,000	3,673	3,863	2,400	−4.2	12.1	11.4
Phenyl bromide...........	1	3,355	3,564	1,961	−4.6	14.4	14.7
	1,000	3,686	3,905	2,201	−4.9		
	2,000	3,975	4,171	2,642	−4.4	11.9	11.0
Pyridine + cetyl bromide: t_1 = 40°C.; t_2 = 60°C. (10)	1	26,655	26,974	21,647	−16.0	−19.4	−12.1
	1,000	26,185	26,680	18,423	−24.8		
	2,000	25,690	26,354	15,298	−33.2		
	3,000	25,349	26,007	15,051	−32.9	−14.1	−14.3
Acetic anhydride + ethyl alcohol: t_1 = 20°C.; t_2 = 40°C.							
In alcohol solution (11, 20).	1	24,177	24,687	16,195	−25.5	−15.3	−12.7
	1,000	23,807	24,380	14,840	−28.65		
	2,000	23,379	23,950	14,443	−28.55		
	3,000	23,015	23,589*	14,032	−28.7	−15.0	−14.8
In toluene solution........	1	23,879	24,498	14,192	−30.95	−10.0	−11.4
	3,000	23,151	23,672	14,997	−26.05		
	5,000		23,269				
	8,500		22,137				

* Extrapolated from 35°C.

TABLE 2—*Concluded*

REACTION		P	$\Delta F^{\ddagger}_{t_1}$	$\Delta F^{\ddagger}_{t_2}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta V^{\ddagger}_{t_1}$	$\Delta V^{\ddagger}_{t_2}$
		atm.						
Ethyl ether + ethyl iodide in alcohol (11, 20): t_1 = 15°C.; t_2 = 30°C.		1	22,631	22,779	19,791	−9.9	−3.6 −2.7	−3.8 −3.5 −1.2 −1.0
		3,000	22,366	22,501	19,774	−9.0		
		5,000	22,234	22,330	20,391	−6.4		
		8,500	22,223	22,231	22,070	−0.53		
		12,000	22,205	22,149	22,317	3.73		
Alkaline hydrolysis of sodium monochloroacetate (20): t_1 = 60°C.; t_2 = 80°C.		1	25,875	26,143	21,547	−13.4	−5.7 −4.6 −4.9 −3.3 −2.4	−6.1 −3.7
		3,000	25,463	25,698	21,550	−11.8		
		5,000	25,241					
		7,600	24,932	25,191	20,620	−13.0		
		8,500	24,860					
		12,000	24,659	24,950	19,814	−14.6		
$2H^+ + Br^- + BrO_3 = HBrO + HBrO_2$ (13): t_1 = 15°C.; t_2 = 25°C.		1	16,509	16,607	13,687	−9.8	2.56 2.97 2.31	2.81 2.48 2.56
		500	16,540	16,641	13,631	−10.1		
		1,000	16,576	16,671	13,840	−9.5		
		1,500	16,602	16,702	13,722	−10.0		

REACTION	CATALYST	P	$\Delta F^{\ddagger}_{t_1}$	$\Delta F^{\ddagger}_{t_2}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta V^{\ddagger}_{t_1}$	$\Delta V^{\ddagger}_{t_2}$
Acid inversion of sucrose (2, 3, 18): t_1 = 15°C.; t_2 = 25°C. (a), 26°C. (b)	0.5 M HCl..	1	18,343	18,088[a]	25,687	25.5	3.6	3.8
		500	18,387	18,134	25,653	25.3		
	0.5 M H_2SO_4.	1	18,767	18,550[b]	24,441	19.7	1.24	1.65
		500	18,782	18,570	24,340	19.3		
	0.5 M Oxalic acid	1	19,530	19,375	23,591	14.1	1.65	0.9
		500	19,550	19,386[b]	23,841	14.9		
	0.5 M Phosphoric acid	1	19,988	19,816	24,942	17.2	−2.8	−2.5
		500	19,954	19,786[a]	24,792	16.8		
	0.5 M Acetic acid	1	21,552	21,390	25,786	14.7	−4.85	4.2
		500	21,492	21,441[b]	22,817	4.6		
	n/16 HCl....	1		20,000[a]				5.0 5.3 4.3
		500		20,060				
		1,000		20,124				
		1,500		20,176				
t_1 = 25°C. t_2 = 45°C.	0.5 M Acetic acid	1	21,875	21,659	25,093	10.8	−0.9 −1.4 0	−2.0 −1.2 0
		500	21,864	21,635	25,276	11.4		
		1,000	21,847	21,620	25,229	11.4		
		1,500	21,847	21,620	25,229	11.4		

on activation are not important, by the use of two simple rules: (*1*) For a monomolecular reaction

$$\Delta V^{\ddagger} = \frac{0.1l^{\ddagger}}{\sum_i l_i + r_1 + r_2 + 1} V \tag{11}$$

where l_1 is the sum of the bond lengths taken in the direction of decomposition, r_1 and r_2 are the covalent radii of the terminal atoms at either end, V is the molal volume, and $l^{\ddagger}$ is the length of the bond which breaks and which, in the activated complex, has lengthened by about 10 per cent. The number 1 added to the denominator is twice the distance from the covalent (or electrovalent) "shell" of the outer atom to the kinetic theory shell of the molecule. This number is taken from the fact that a hydrogen atom in water is about 0.8 Å. nearer the oxygen atom to which it is covalently bonded than to the next nearest oxygen atom (16), so that this distance will, in general, be somewhat larger than and not differ much from 1 Å.

(*2*) For bimolecular reactions

$$- \Delta V^{\ddagger} = \frac{1}{\sum_i l_i + \sum_j r_j + 2} \sum V \tag{12}$$

In equation 12 we assume that, from the sum of the molal volumes of the reactants, ΣV, we squeeze out the 1 Å. between them when the activated complex is formed. $\Sigma_i l_i$ is the sum for both molecules of the sum of the interatomic distances between the remote end and the reacting end of each molecule, and the r's are the covalent (or ionic, if the reacting atom is charged as, for example, oxygen in HO⁻) radii of the end atoms and of the reacting atoms of the molecules.

In table 3 we compare measured values of $\Delta V^{\ddagger}$ with values calculated by means of equation 11 or 12.

Two reactions are particularly worthy of comment. Moesveld (13) studied the kinetics of the reaction

$$HBr + HBrO_3 \rightarrow HBrO + HBrO_2$$
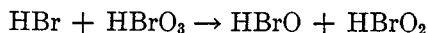
in aqueous solution to pressures of 1500 atmospheres. This reaction has been shown by Judson and Walker (12) to be of the fourth order. Ordinarily it might be expected that pressure would accelerate its rate. The reverse effect was found. In this reaction, however, four ions combine to form two molecules of weak electrolyte, so that the formation of the activated complex is accompanied by the liberation of electrically bound solvent to an extent which overbalances, though not greatly, the decrease in volume otherwise to be expected. The net effect amounts to a volume

TABLE 3

Comparison of experimental and calculated values of $\Delta V^{\ddagger}$

REACTION AND REFERENCE	PRESSURE RANGE	$\Delta V^{\ddagger}$ EXPERIMENTAL	$\Delta V^{\ddagger}$ CALCULATED
	atmospheres	cc.	cc.
Decomposition of methylallylbenzyl-ammonium bromide (20).........	1–3000	3.4	3.5 for breaking methyl bond 2.7 for breaking any other bond
Pyridine + ethyl iodide (11).......	1–3000	−16.3	−15.8
Pyridine + cetyl bromide (10)......	1–1000	−12.5	−12.3
Acetic anhydride + ethyl alcohol (20)..	1–1000 (in alcohol)	−14.0	−13.3 for 1 C_2H_5-OH per 1 anhydride
	1–3000 (in toluene)	−12.2	
Alkaline hydrolysis of $ClCH_2COO^-$ (20)	1–3000	−6.	−8.
Ethoxide + ethyl iodide (20).......	1–3000	−4.	−11.
Alkaline saponification of ethyl acetate (4)...........	250–500	−5.5	−11.
Ethyl o-methylcin-namate (14).......	1–500	−14.0 (in 31% alcohol) −12.4 (in 42% alcohol)	−12.3
Cinnamyl cinnamate (15)..............	1–1500	−14.5	−11.
Ethyl o-methoxycin-namate (15).......	1–1500	−15.5 (in 25% alcohol) −12.1 (in 38% CH_3OH) −16.8 (in 28% acetone) −16.2 (in 20% C_3H_7OH)	−12.7
Ethyl benzoate (15)..	1–1500	−13.6	−10.7
Ethyl o-methoxyben-zoate (15).........	1–1500	−11.3 (in 7% alcohol) −14.2 (in 2.5% pyridine)	−13.7
Benzyl benzoate (15).	1–1500	−17.9	−14.7
Ethyl anthranilate (15)..............	1–1500	−10.4	−11.6
Linalyl acetate (15)..	1–1500	−16.2	−17.4
Bornyl acetate (15)..	1–1500	−24.5 (in 31% alcohol) −22.1 (in 41% alcohol) −24.5 (in 19% C_3H_7OH) −20.4 (in 3.5% pyridine) −25.0 (in water)	−20.1
$2H^+ + Br^- + BrO_3^-$ (13)..............	1–500	2.6	
Acid inversion of sucrose (2, 3, 18)..	1–500	1 to 5 in HCl, H_2SO_4, or oxalic acid −2 to −5 in phosphoric or acetic acid	

increase of between 2 and 3 cc. (table 2). We, therefore, expect that in this case ΔV of reaction will be in the same direction as $\Delta V^{\ddagger}$ of activation and will be a little larger. The other reaction is the acid inversion of cane sugar. Cohen and de Boer (3; see, also, 2 and 18) have found a small but unequivocal pressure effect on the rate. In this reaction the effect of pressure on the rate depends on the nature of the catalyst. Specifically, for example, pressure increases the rate in the presence of acetic acid but decreases it in the presence of hydrochloric acid. This result indicates that either chloride ion or acetate ion, or both, are built into the activated complex, or their presence would not affect $\Delta V^{\ddagger}$. But if they are to be built into the activated complex they must release some of their water of hydration, which should be more in the case of chloride ion than of acetate ion. Thus one might expect that $\Delta V^{\ddagger}$ should be more positive for chloride ion than for acetate ion, as in fact it is. In no case is the effect large, and the next volume change results from a balance between loss of volume when sucrose, water, and catalyst combine into activated complex, and a volume increase due to the opening up of the large sucrose molecule on activation. The significance of this second factor may be inferred from the fact that $\Delta S^{\ddagger}$ is in all cases positive.

Polymerization reactions have been studied at high pressures by Tammann and Pape (19) as well as by Conant *et al.* (5, 6). Pressure has a very large accelerating effect on the rate. The necessity of well-controlled catalytic environment renders the data slightly less trustworthy for quantitative interpretation, but the rate of polymerization of isoprene under roughly comparable conditions increases nearly 6000 times at room temperature between pressures of 2000 and 18,000 atmospheres, according to measurements of Conant and Tongberg, and the rates are nearly proportional to the fourth power of the pressure through this entire pressure range. Tammann and Pape, working at higher temperatures and through the pressure range of about 1000 to 3000 atmospheres, found that under these conditions the rates of polymerization of isoprene, styrene, and dimethylbutadiene increase as the second power of the pressure in the first two cases and as the fourth power in the case of dimethylbutadiene. The data of Conant and those of Tammann for isoprene seem quite comparable, since temperature extrapolation of the rate constant at 2000 atmospheres, using the mean of the values of activation given by Conant and Tongberg for room temperature and by Tammann and Pape for 150°C., bring the two values of the rate constant to within a factor of about 2, though the initial constants differed by over 2×10^{4}.

It is generally accepted that these polymerization reactions have chain mechanisms. Their rates may be instructively formulated in terms of the factors which effect the starting and the breaking of the chains. For the

rate of reaction of a radical (i.e., the chance that, in unit time, a chain will be broken), we write

$$1/\tau_{\text{ave.}} = C_w k_2 + \sum_i C_{b_i} k_{1_i} \qquad (13)$$

where C_w is the effective concentration of wall molecules (i.e., the number of reactive surface atoms per cubic centimeter of reacting medium) and C_b is the concentration of any other molecular species which inhibits the reaction by means of breaking the chain. k_2 and the k_1's are the corresponding rate constants. k_2 will depend on the nature and shape of the wall and the rate of diffusion to the wall; k_1 will depend on the particular reaction and on the diffusion velocity. τ is the life period of the chain. We use an average value since, for such reactions as polymerizations, increase in chain length involves actual increase in the size of the reacting radical, and thus the older the chain the smaller the chance of breaking due to its diffusion (e.g., to the wall).

The measured rate of reaction would then be

$$k' = C_r k_3 \tau_{\text{ave.}} = \frac{C k_4 k_3}{C_w k_2 + \sum_i C_{b_i} k_{1_i}} \qquad (14)$$

where C_r is the concentration of radicals, and k_3 is the rate constant for the growth of a chain. For C_r we write $C k_4$, where C is the concentration of the parent substance and k_4 measures the rate of initiation of chains. If k_1, k_2, k_3, and k_4 are independent of C, the reaction will be of the first order, as is observed. Positive catalysts,—as, for example, peroxide in the polymerization of isoprene,—probably act by increasing k_4. In general, negative catalysts may act as chain breakers, increasing the denominator of the right-hand side of equation 14, or they may presumably decrease the values of either k_3 or k_4.

Conant and Tongberg give the activation energy for polymerization of isoprene at room temperature and 2000 atmospheres as about 24,000 calories, whereas the data of Tammann and Pape at 2000 atmospheres indicate an activation energy at 150°C. of about 17,300 calories. From equation 14 it is seen that the measured value of the activation energy is the difference between the sum of those energies characteristic of k_3 and k_4 and some sort of average of the analogous energies characteristic of k_2 and the k_1's. It is quite possible that the dominant chain-breaking mechanism may be an entirely different one at high temperatures than at lower temperatures, so that one need not be surprised at large temperature variation of activation energy.

While values of $\Delta S^{\ddagger}$ may not have the same significance for these reactions as for the others treated in this paper, it may be pointed out that,

from data available, they are negative and rather large, ranging from -30 to -50 units.

The effect of pressure on polymerization rates is in a sense slightly easier to analyze than is that of temperature. Naturally, increasing the pressure increases C and the C_b's and perhaps C_w, but such effects are small compared with the effect on k' itself. The somewhat complicated net pressure effect on the polymerization rate will manifest itself as simple changes in the various specific rate constants on the right-hand side of equation 14.

If we accept the idea of Conant and Peterson as to the function of peroxide decomposition in initiating chains in isoprene polymerization, and assume some analogous mechanism in the general case, then we expect k_4 to be nearly independent of pressure, though it should decrease slightly. This would accord with the findings of Williams, Perrin, and Gibson (20) as to the effect of pressure on the monomolecular decomposition of phenyl-benzylallylmethylammonium bromide, the rate of which decreases about 33 per cent on going from 1 atmosphere to 3000 atmospheres. We may, therefore, think of k_4 as nearly independent of pressure or as decreasing as a small fractional power of the pressure.

On the evidence of the effect of pressure on the rates of those bimolecular reactions for which data are available and for which, on the average, k' increases about as the first power of pressure (starting with an initial pressure of at least 500 atmospheres), we expect k_3 to vary about as the first power of the pressure. k_2 and the k_1's should depend on pressure in much the same way as does fluidity. Now we find that, in the range of about 5000 to 12,000 atmospheres at 30°C., viscosity varies nearly as the cube of the pressure. This power is an average based on data for the three hydrogen-bonded liquids n-propyl alcohol, isobutyl alcohol, and glycerol, and the three more normal liquids n-pentane, ethyl bromide, and carbon disulfide. We would then expect that the speed of polymerization at room temperature would increase about as $P^{0\ +\ 1\ +\ 3}$ or as P^4, in good agreement with the data of Conant and Tongberg for isoprene polymerization at room temperature. The measurements of Tammann and Pape on the same reaction were made at higher temperatures (*ca.* 150°C.) and lower pressures (1000 to 3000 atmospheres in place of the 2000 to 18,000 atmospheres covered by Conant and Tongberg). In the pressure range 1000 to 3000 atmospheres the viscosities of the six liquids enumerated above vary, on the average, with $P^{0.9}$ at 30°C., changing to $P^{0.8}$ at 75°C., and presumably to a somewhat lower power of pressure at 150°C. This is entirely consistent with the finding, by Tammann and Pape, of a rate of isoprene polymerization increasing as P^2 under their experimental conditions.

According to the mechanism pictured above for polymerization reactions, the calculated value of $\Delta V^{\ddagger}$ will be a composite $\Delta V^{\ddagger}$ for diffusion and

$\Delta V^{\ddagger}$ for polymeric addition. Now the density of the isoprene monomer is 0.68, while that of the polymerized material is 0.9. Thus the complete reaction involves a volume decrease of 24.5 cc. per isoprene unit. The formation of the activated complex would involve slightly less. On the basis of equation 11 it would involve a decrease of 0.9 of 24.5, or 22 cc., per isoprene unit. In diffusion or viscous flow the volume increase on activation averages about one-seventh the volume of the diffusing segment. Thus if X be the number of isoprene units in the diffusing segment, then

$$\Delta V^{\ddagger}_{\text{meas.}} - 22X = \frac{V_c X}{7} \tag{15}$$

V_c is the volume per isoprene unit of the condensed chain. Since there are two double bonds in isoprene, we use 22 cc. as the volume shrinkage for formation of the activated complex between two reacting units in place of twice this value if there were only one point of condensation per isoprene unit. For numerical substitution we should know the value of $\Delta V^{\ddagger}_{\text{meas.}}$ at low pressures (since relative compressibilities of monomer and polymer are not known over a pressure range). The data of Tammann and Pape give $\Delta V^{\ddagger} = -66$ cc. for the pressure range 650 to 1140 atmospheres, and $\Delta V^{\ddagger} = -266$ cc. for the pressure range 1 to 1500 atmospheres. These values of $\Delta V^{\ddagger}$ correspond, respectively, to about four and twenty-two isoprene units as constituting the diffusing segment.[2] The former value is probably more nearly correct, since the experimental pressure effect on k' at 1 atmosphere is highly questionable.

In the case of styrene, the density of the monomer being 0.902 and that of the polymer "1.043 to 1.056" (19), we take 1.05 as the density of the polymer and obtain a volume decrease in going from polymer to activated complex of 14 cc. per styrene unit. For measured values of $\Delta V^{\ddagger}$, Tammann's data yield -84 cc. for the pressure range 740 to 1300 atmospheres, and -327 cc. for the pressure range 1 to 1500 atmospheres. These values of $\Delta V^{\ddagger}$ correspond respectively to about four and twenty-one styrene units as constituting the diffusing segment, the former value being probably more nearly true.

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