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due to the differences in electronic configuration and thus differences in polarizabilities of these molecules. In this work, the polarizability differences are taken into account in the calculation of the adsorption potential as the mean polarizability and the polarizability ratio of the adsorbate molecule (α_{i1}/α_{i3}) assigned to each C force center of the molecule, derived from the corresponding molecular experimental data. The predicted s value for phenanthrene/anthracene adsorption on graphite is 1.44 when polarizability data are taken from Lefevre et al.[39] and 1.55 from Schuyer et al.[40] instead of 1.23 for the experimental value as measured by gas-adsorption chromatography. These calculations demonstrate how sensitive the model is to the value accepted for the mean polarizability of the carbon force center of the adsorbate molecule.

Conclusion

These results show that the anisotropic adsorption potential model of Meyer and Dietz,[14,15] when applied to the molecular theory of adsorption, predicts with good agreement, at least as well as the empirical adsorption potential laws, the thermodynamic functions of adsorption of alkanes and aromatic hydrocarbons on graphite.

The adsorption potential which takes into account the high anisotropic polarizability of graphite can be expressed with a good approximation by a Lennard-Jones (12–6) potential. The Kirkwood–Müller constant used for isotropic adsorption potential calculations on graphite is $^4/_3$ larger than the attractive constant which assumes that the polarizability in the direction normal to the basal plane is zero. Therefore, adsorption potential laws which use the Kirkwood–Müller attractive constants to predict B_{AS} and q_{st} values for the adsorption on graphite give results which are too large.

The relative retention of geometrical isomers are equal when calculated with the anisotropic or isotropic potential models if the same polarizability and diamagnetic susceptibility increments are assigned to the adsorbate force centers. Similarly the conclusions of Battezzati et al.[11] which cencern the most stable equilibrium adsorbate conformations on graphite still hold with the anisotropic adsorption potential model.

Finally, this work shows that correct knowledge of the polarizability of the adsorbate molecule and the structural properties of the adsorbed layers is of great importance in order to derive the constants of the adsorption potential laws.

Registry No. Graphite, 7782-42-5.

New Simple Functions To Describe Kinetic and Thermodynamic Effects of Pressure. Application to *Z–E* Isomerization of 4-(Dimethylamino)-4′-nitroazobenzene and Other Reactions

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Two simple three-parameter equations are proposed as functions to describe kinetic and thermodynamic effects of pressure. The functions are found to reproduce experimental results more accurately than the most frequently used quadratic equation. The estimated activation volumes at zero pressure are almost independent of the experimental pressure range for most of the reactions examined and their standard deviations are reasonably small. The activation volumes at infinite pressure are, in many cases, in fairly good agreement with the intrinsic activation volumes calculated by an independent procedure.

Introduction

Activation volume has been proved to be an effective tool to elucidate organic as well as inorganic reaction mechanisms.[1-3] For this purpose, activation volume at zero pressure, $\Delta V_0^{\ddagger}$, which is practically equal to the value at 1 bar, is usually employed. To estimate $\Delta V_0^{\ddagger}$ is a simple task when the value is independent of pressure. The pressure dependence of a rate constant can be described by eq 1 and $\Delta V_0^{\ddagger}$ is given by $-bRT$ as shown in eq 2,

$$\ln (k_P/k_1) = a + bP \tag{1}$$

$$\Delta V_0^{\ddagger} = -RT(\partial \ln k_P/\partial P)_T = -bRT \tag{2}$$

where k_P is the rate constant at pressure P. However, in many reactions studied so far, $\ln k_P$ turned out to be a nonlinear function of pressure. In such instances, we need a suitable function to describe the pressure dependence of $\ln k_P$. Several equations have been proposed and compared. For example, Hyne and his coworkers[4] analyzed their data on the hydrolysis of benzyl chloride in water by eq 1 and 3–7 and concluded that all the functions

$$\ln (k_P/k_1) = a + bP + cP^2 \tag{3}$$

$$\ln (k_P/k_1) = a + bP + cP^2 + dP^3 \tag{4}$$

$$\ln (k_P/k_1) = bP + cP^2 \tag{5}$$

$$\ln (k_P/k_1) = aP + bP^{1.523} \tag{6}$$

$$\frac{\ln (k_{P_{i+1}}/k_{P_i})}{P_{i+1} - P_i} = a + \frac{b}{2}(P_{i+1} + P_i) \tag{7}$$

except eq 1 gave essentially the same activation volume. Kelm and Palmer[5] tried eq 3, 4, 6, 8, and 9 for data on a Diels–Alder

$$\ln (k_P/k_1) = a + b[1 - \exp(-cP)] \tag{8}$$

$$\ln (k_P/k_1) = a + bP/(c + P) \tag{9}$$

reaction and a ligand substitution reaction. They noticed that the quadratic equation 3 tends to underestimate the activation volume but none of the functions appears to be superior in describing the experimental data. Because of its mathematical simplicity, the quadratic equation has been used by the over-

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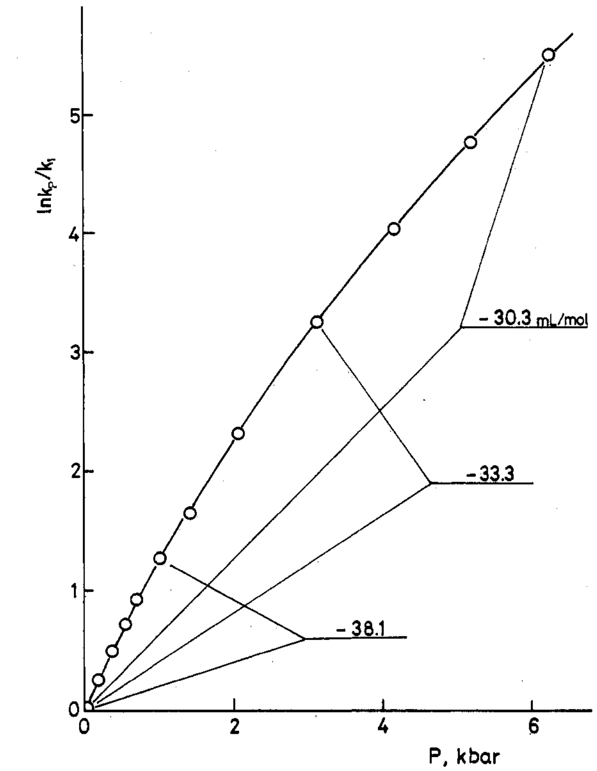

Figure 1. Activation volumes at zero pressure for the reaction between isoprene and maleic anhydride calculated by the quadratic equation.

TABLE I: First-Order Rate Constants for the Thermal Isomerization of (*Z*)-4-(Dimethylamino)-4'-nitroazobenzene in Chloroform at 25 °C

P, kbar	*k*, s^{-1}	*P*, kbar	*k*, s^{-1}
0.001	0.180 ± 0.002	2.100	0.853 ± 0.004
0.300	0.241 ± 0.003	2.400	1.012 ± 0.008
0.600	0.311 ± 0.002	2.700	1.183 ± 0.016
0.900	0.396 ± 0.005	3.000	1.364 ± 0.008
1.200	0.486 ± 0.005	3.300	1.577 ± 0.008
1.500	0.592 ± 0.001	3.600	1.800 ± 0.007
1.800	0.716 ± 0.002	3.900	2.029 ± 0.024

whelming majority of investigators and the analyses by Hyne and Kelm mentioned above seem to validate this choice. However, the equation has two drawbacks. Firstly, whenever we use eq 3 for nonlinear kinetic or thermodynamic effects of pressure, the resultant equation yields an unrealistic prediction that the pressure effect changes its sign somewhere at higher pressure ranges and becomes indefinitely large at infinite pressure. Suppose we have a reaction that is accelerated by pressure. The estimated parameter *c* is almost inevitably negative and the function becomes a parabola which has a maximum outside the experimental pressure range. The second and more serious problem from the standpoint of estimating $\Delta V_0^{\ddagger}$ is the fact that $\Delta V_0^{\ddagger}$ depends on the pressure range adopted; in other words, the slope at zero pressure decreases as more points from the upper pressure area are included in the calculation. This has been known for many years among high-pressure kineticists and the importance of data collection in the lower pressure region has been well recognized. A case in point is illustrated in Figure 1. The reaction studied was the Diels–Alder reaction between isoprene and maleic anhydride.[6] Judging from the smoothness of the plot, the data quality is excellent. The $\Delta V_0^{\ddagger}$ value decreases consistently when the points at higher pressures are included in the calculation. Namely, when the calculation is performed on the basis of the rate constants between 0.001 and 1 kbar, $\Delta V_0^{\ddagger}$ is −38.13 ± 0.57 mL/mol but the value becomes −30.29 ± 0.74 mL/mol when all the data are used. This dependence of activation volume on the experimental pressure range could cause problems when we want to compare the results from different research groups because usually the experimental pressure range and, in most cases, the pressure intervals are different and the activation volumes obtained cannot be compared quantitatively. Therefore, it is highly desirable to have a function that gives constant activation volume at zero pressure despite the different pressure ranges adopted in the experiment.

Discussion

New Functions. New functions are required to satisfy the following conditions: (i) They must reproduce experimental results with good accuracy. (ii) Their first derivative with respect to pressure at $P = 0$ must be independent of the pressure range and its standard deviation must be reasonably small. (iii) The slope should become constant at infinite pressure. (iv) And ideally, the equations should be mathematically simple. The following two functions satisfy the last two conditions:

$$\ln (k_P/k_1) = aP + bP/(1 + cP) \tag{10}$$

$$\ln (k_P/k_1) = aP + b \ln (1 + cP) \tag{11}$$

Both of them have three adjustable parameters as does the quadratic equation 3 and the forms are relatively simple. The activation volumes at zero pressure are given by eq 12 and 13, respectively

$$\Delta V_0^{\ddagger} = -(a + b)RT \tag{12}$$

$$\Delta V_0^{\ddagger} = -(a + bc)RT \tag{13}$$

and they can be directly calculated by changing eq 10 and 11 as follows:

$$\ln \frac{k_P}{k_1} = -\left(\frac{\Delta V_0^{\ddagger}}{RT} + b\right)P + \frac{bP}{1 + cP} \tag{14}$$

$$\ln \frac{k_P}{k_1} = -\left(\frac{\Delta V_0^{\ddagger}}{RT} + bc\right)P + b \ln (1 + cP) \tag{15}$$

Since the first derivative of $\ln k_P$ with respect to pressure becomes *a* at infinite pressure in both of the equations, the third condition mentioned above is also satisfied. In order to assess eq 10 and 11, we ought to select a simple reaction system, because, if we choose, for example, a multistep reaction, the kinetic equation becomes complicated and we must estimate more than one activation volume from one set of data.[7] It introduces unnecessary complication and makes the assessment of our equations difficult. Thermal *Z–E* isomerization of 4-(dimethylamino)-4'-nitroazobenzene, hereafter referred to as NMe_2-NO_2-AB, is one of the most suitable reactions for the present purpose. It is a simple one-step reaction which proceeds via the dipolar transition state, **1**, in benzene and more polar solvents.[8] There is little possibility that it involves either a preequilibrium or a backward reaction. And the reaction is highly accelerated by pressure because of the large increase in solvation (electrostriction) in the activation step. The rate constant can be measured accurately by flash spectroscopic technique. Table I lists the rate constants for the isomerization in chloroform at 25 °C and the results are illustrated in Figure 2. The activation volumes, $\Delta V_0^{\ddagger}$, estimated by eq 3, 10, and 11 and the residual sum of squares, ss, for each equation

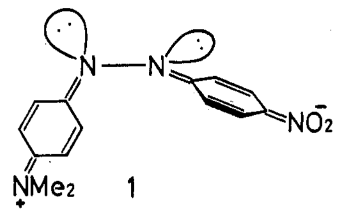

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TABLE II: Activation Volumes for the Thermal Isomerization of (*Z*)-4-(Dimethylamino)-4′-nitroazobenzene in Chloroform Estimated by Various Equations along with the Parameters and the Residual Sum of Squares for Each Equation[a]

eq	$\Delta V_0^\ddagger$, mL/mol	10^4(ss)	*a*	*b*	*c*
3	−21.62 ± 0.34	30.66	0.03151 ± 0.01168	0.8722 ± 0.0139	−0.06750 ± 0.00344
10	−24.99 ± 0.25	2.838	0.1977 ± 0.0334	0.8105 ± 0.0249	0.2325 ± 0.0232
11	−25.14 ± 0.26	2.518	0.05706 ± 0.04155	2.266 ± 0.321	0.4223 ± 0.0459

[a] Pressure in kbar.

TABLE III: Dependence of the Activation Volume (mL/mol) at Zero Pressure on the Upper Pressure Limit in the Thermal Isomerization of (*Z*)-4-(Dimethylamino)-4′-nitroazobenzene

press. limit, kbar	eq 3	eq 10	eq 11
1.5	−24.61 ± 0.36	−25.47 ± 0.57	−25.48 ± 0.59
2.1	−23.56 ± 0.45	−25.89 ± 0.42	−25.97 ± 0.46
2.7	−22.72 ± 0.44	−25.80 ± 0.29	−25.93 ± 0.32
3.3	−22.13 ± 0.38	−25.36 ± 0.27	−25.50 ± 0.29
3.9	−21.62 ± 0.34	−24.99 ± 0.25	−25.14 ± 0.26

are given in Table II along with the values for the parameters *a*, *b*, and *c*. Obviously, the new equations are better than eq 3 in describing the experimental results. The ss is more than 1 order smaller for eq 10 and 11. The situation can be seen clearly in the lower half of Figure 2, where the differences between the calculated and experimental values of ln k_P are plotted against pressure for eq 3 and 11. The results obtained by eq 10 were very close to the ones obtained by eq 11 and, therefore, they were omitted in the figure. The differences are much smaller for eq 11 and no systematic deviation from the experimental value was observed. Table III lists the $\Delta V_0^\ddagger$ values estimated by eq 3, 10, and 11 on the basis of the rate constants from various pressure ranges. The activation volume decreases when increasing the upper pressure limit in the quadratic equation, but it is almost constant in the new equations. The standard deviations of $\Delta V_0^\ddagger$ are of the same magnitude in the three equations. Therefore, these two functions seem to satisfy the four conditions mentioned above and their application to other reactions is warranted.

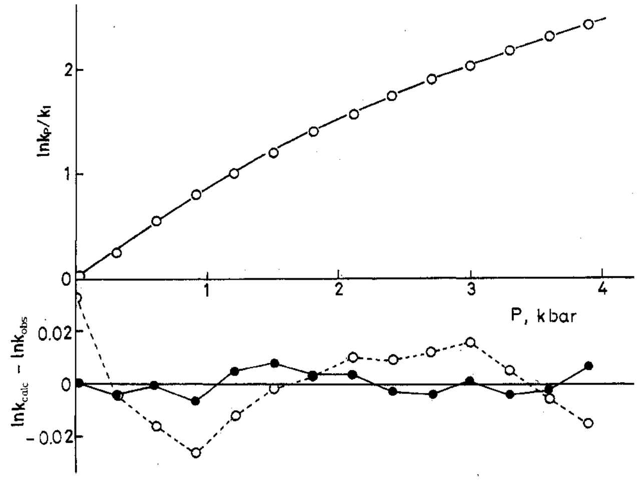


Figure 2. Pressure effects on the thermal isomerization of (*Z*)-NMe$_2$-NO$_2$-AB and the differences between the calculated and observed rate constants: (---○---) eq 3; (−●−) eq 11.

Application to Other Simple Reactions. The calculations were performed on the Diels–Alder reaction studied by Grieger and Eckert[6] (Figure 1). The activation volumes and ss values are given in Tables IV and V. The new functions appear to reproduce the

TABLE IV: Activation Volumes for the Diels–Alder Reaction between Isoprene and Maleic Anhydride in Ethyl Acetate[a] Estimated by Various Equations along with the Parameters and the Residual Sum of Squares for Each Equation[b]

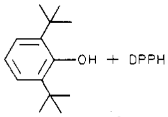
eq	$\Delta V_0^\ddagger$, mL/mol	10^3(ss)	*a*	*b*	*c*
3	−30.29 ± 0.74	24.55	0.07616 ± 0.02786	1.182 ± 0.029	−0.05192 ± 0.00472
10	−37.09 ± 0.61	2.426	0.5359 ± 0.0336	0.9120 ± 0.0203	0.2645 ± 0.0338
11	−37.48 ± 0.68	2.318	0.4158 ± 0.0435	1.989 ± 0.339	0.5263 ± 0.0802
16	−39.40 ± 1.36	2.314	0.1751 ± 0.0186	4.292 ± 1.791	

[a] Reference 6. [b] Pressure in kbar.

TABLE V: Dependence of the Activation Volume (mL/mol) at Zero Pressure on the Upper Pressure Limit in the Diels–Alder Reaction between Isoprene and Maleic Anhydride

press. limit, kbar	eq 3	eq 10	eq 11	eq 16
1.0	−38.13 ± 0.57	−36.56 ± 0.61	−38.33 ± 2.05	−40.00 ± 6.74
2.1	−35.49 ± 0.77	−38.66 ± 0.88	−38.73 ± 0.97	−40.90 ± 3.21
3.1	−33.28 ± 0.90	−39.19 ± 0.71	−39.48 ± 0.88	−40.85 ± 2.28
4.1	−32.45 ± 0.70	−36.60 ± 0.80	−37.89 ± 0.86	−39.10 ± 1.37
5.2	−31.59 ± 0.62	−36.74 ± 0.66	−37.00 ± 0.69	−38.16 ± 0.96
6.2	−30.29 ± 0.74	−37.09 ± 0.61	−37.48 ± 0.68	−39.40 ± 1.36

TABLE VI: Activation Volumes (mL/mol) for Various Reactions Estimated by Different Equations and the Residual Sum of Squares for Each Equation

				eq 3		eq 10		eq 11		
reaction	solvent	*T*, °C	*P*,[a] kbar	$\Delta V_0^\ddagger$	10^4(ss)	$\Delta V_0^\ddagger$	10^4(ss)	$\Delta V_0^\ddagger$	10^4(ss)	ref
$PhCH_2Cl + H_2O$	H_2O	30	6.9	−8.44 ± 0.76	9.016	−8.93 ± 0.11	6.858	−8.94 ± 0.11	6.812	4
$Et_3N + EtI$	$PhNO_2$	50	2.0	−26.00 ± 0.57	4.117	−28.22 ± 0.78	1.149	−28.28 ± 0.87	1.198	10
TCNE[b] + $BuOCH{=}CH_2$	MeCOMe	30	2.0	−35.55 ± 1.31	26.65	−43.64 ± 0.70	0.6281	−44.26 ± 0.76	0.5152	11
 OH + DPPH[c]	PhMe	25	2.0	−13.44 ± 0.43	5.124	−14.50 ± 1.13	4.774	−14.60 ± 1.29	4.745	12
$Co(NH_3)_5Cl^{2+} + H_2O$	H_2O	25	4.1	−9.92 ± 0.47	23.58	−13.44 ± 1.02	6.064	−13.87 ± 1.19	5.399	13
Pt(dien)Br$^+$[d] + OH^-	H_2O	25	1.5	−14.67 ± 0.78	7.502	−20.89 ± 0.84	0.5954	−21.39 ± 0.99	0.5609	14

[a] The highest pressure. [b] Tetracyanoethylene. [c] Diphenylpicrylhydrazyl. [d] Bromodiethylenetriamineplatinum(II).

TABLE VII: Ionization Volumes (mL/mol) Estimated by Various Equations and the Residual Sum of Squares for Each Equation

acid or base	solvent	T, °C	P,[a] kbar	eq 3		eq 10		eq 11		eq 18		ref
				ΔV_0	10^4(ss)	ΔV_0	10^4(ss)	ΔV_0	10^4(ss)	ΔV_0	10^4(ss)	
H_2O	H_2O	25	7.8	−18.76 ± 0.36	53.34	−21.03 ± 0.32	8.739	−21.11 ± 0.33	8.088	−21.23 ± 0.15	9.361	17
AcOH	H_2O	25	3.0	−10.78 ± 0.17	1.072	−11.52 ± 0.19	0.1780	−11.54 ± 0.21	0.1886	−11.08 ± 0.09	0.5994	18
AcOH	H_2O	150	3.0	−24.78 ± 0.62	6.922	−27.30 ± 0.79	1.615	−27.35 ± 0.87	1.693	−26.40 ± 0.31	2.460	18
H_2CO_3	H_2O	25	2.0	−27.06 ± 0.13	0.7139	−27.42 ± 0.21	0.5661	−27.43 ± 0.21	0.5644	−27.24 ± 0.07	0.6316	19
Et_3N	MeOH	30	1.6	−46.73 ± 0.95	14.64	−51.67 ± 0.95	2.381	−51.80 ± 1.06	2.529	−49.65 ± 0.45	5.196	20

[a] The highest pressure.

TABLE VIII: Pressure Range Dependence of the Ionization Volume (mL/mol) at Zero Pressure for Acetic Acid in Water at 25 °C[a]

press. limit, kbar	eq 3	eq 10	eq 11	eq 18
2.0	−11.20 ± 0.10	−11.25 ± 0.20	−11.26 ± 0.20	−11.33 ± 0.07
2.4	−11.02 ± 0.15	−11.43 ± 0.25	−11.44 ± 0.26	−11.22 ± 0.08
3.0	−10.78 ± 0.17	−11.52 ± 0.19	−11.54 ± 0.21	−11.08 ± 0.09

[a] Reference 18.

experimental data more precisely. The ss values are smaller and $\Delta V_0^\ddagger$ is almost independent of the pressure range employed. Recently, El'yanov and Gonikberg[9] proposed a new three-parameter equation, eq 16, as a description of the kinetic effects of

$$RT \ln \frac{k_P}{k_1} = -\Delta V_0^\ddagger \left[(1 + a)P - \frac{a}{b}(1 + bP) \ln (1 + bP) \right] \tag{16}$$

pressure on nonionic reactions. Tables IV and V include the results obtained by this equation. The equation gives essentially the same ss value as eq 11. However, it is mathematically more complicated than eq 10 and 11 and the standard deviations in $\Delta V_0^\ddagger$ tend to be larger than in eq 10 and 11 especially when the data base is small. In addition, it shows the same drawback as the quadratic equation when the function is extrapolated to the high-pressure region. The activation volume is given by eq 17 and it becomes

$$\Delta V_P^\ddagger = \Delta V_0^\ddagger [1 - a \ln (1 + bP)] \tag{17}$$

zero at $P = (1/b)[\exp(1/a) - 1]$, which is equal to 70.3 kbar for the reaction between isoprene and maleic anhydride, and it continues to increase with pressure. Therefore, the simpler equation 11 (or 10) seems to be more suitable, at least, when the data base is small or the extrapolation of the pressure effect is intended.

In Table VI, the three equations 3, 10, and 11 are compared for several other reactions. It is true that eq 3 gives smaller $\Delta V_0^\ddagger$ and larger ss values. Since the new equations reproduce the experimental results more accurately, and reasonable activation volumes with relatively small standard deviations are obtained in various types of reactions, it can reasonably be concluded that either eq 10 or 11 is preferable to the widely used quadratic equation in the analysis of kinetic effects of pressure. The most impressive example is the hydrolysis of $Pt(dien)Br^+$. In this reaction, the activation volume estimated by the quadratic equation is much smaller than the average activation volume between 1 and 125 or 250 bar (−18.91 and −16.74 mL/mol, respectively). On the other hand, the values by the new functions are a few mL/mol more negative than the average value for 1 and 125 bar as expected from the general tendency of decreasing activation volume with increasing pressure.

Ionization Equilibria. The success of eq 10 and 11 in analyzing kinetic data for ionic reactions encourages us to extend their application to ionization equilibria because most of the negative reaction volumes observed in ionization are the results of electrostriction as, for example, in the isomerization of NMe_2-NO_2-AB. For ionization equilibria, El'yanov and Hamann[15] proposed eq 18 and Nakahara[16] showed that the equation could

$$\ln (K_P/K_1) = bP/(1 + cP) \tag{18}$$

be derived on the basis of the continuum model of liquid and the Dunn–Stokes equation for the pressure dependence of the dielectric constant of a liquid. This equation contains only two adjustable parameters and implies that the ionization volume becomes zero at infinite pressure. However, this assumption of zero ΔV_∞ would not hold true in some ionization reactions where bond formation takes place as in the first ionization of carbonic acid.

$$CO_2 + H_2O \rightleftarrows HCO_3^- + H^+ \tag{19}$$

Since our equations contain one more adjustable parameter, they would be more versatile and more effective in describing experimental results. Calculations were performed for a number of ionizational data and several representative examples are shown in Table VII. In all cases listed, the quadratic equation gives the poorest results. El'yanov and Hamann's two-parameter equation presents much better results, but the residual sum of squares is always greater than that for eq 10 or 11. It is impossible to tell whether either eq 10 or 11 is better for the calculation of ionization volume; the two functions give virtually the same results.

An example of the dependence of the ionization volume at zero pressure on the pressure ranges are shown in Table VIII. Although eq 10 and 11 yield ΔV_0 which varies slightly when the equilibrium constants from the upper pressure region are included, the variations are small and may not impose serious problems in the comparison of the pressure effects from different sources.

Implication of Parameter a. As can be seen from the following equation, parameter a in eq 10 and 11 is directly related to the activation (or reaction) volume at infinite pressure, $\Delta V_\infty^\ddagger$:

$$\lim_{P\to\infty} [-RT(\mathrm{d} \ln k_P/\mathrm{d}P)] = \Delta V_\infty^\ddagger = -aRT \tag{20}$$

This parameter may be considered equal to the intrinsic activation volume, $\Delta V^\ddagger_{\mathrm{int}}$, in eq 21, where $\Delta V^\ddagger_{\mathrm{solv}}$ is the volume change of

$$\Delta V^\ddagger = \Delta V^\ddagger_{\mathrm{int}} + \Delta V^\ddagger_{\mathrm{solv}} \tag{21}$$

the solvent molecules during activation, and $\Delta V^\ddagger_{\mathrm{int}}$ is usually referred to as the volume change of the reacting molecules

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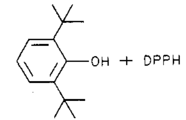
TABLE IX: Comparison of the Activation Volume at Infinite Pressure and the Intrinsic Activation Volume (mL/mol)

reaction	T, °C	solvent	$\Delta V_\infty^\ddagger$ or $\Delta V^\ddagger_{int}$ eq 10	 eq 11	 eq 23	ref
$Et_3N + EtI$	50	$PhNO_2$	−14.2 ± 2.4	−11.7 ± 3.3	−8.7 ± 0.6	10
$TCNE + BuOCH{=}CH_2$	30	MeCOMe	−16.1 ± 0.8	−12.6 ± 0.9	−9.9 ± 0.5	11
isomerization of NMe_2-NO_2-AB	25	$CHCl_3$	−4.9 ± 0.8	−1.4 ± 1.0	−7.7 ± 0.2	this work
$PhCH_2Cl + H_2O$	30	H_2O	+4.4 ± 2.9	+7.8 ± 3.8	−2.4 ± 0.2	4
$CH_2{=}C(Me)CH{=}CH_2$ + MA[a]	35	AcOEt	−13.7 ± 0.9	−10.7 ± 1.1		6
	25	PhMe	−8.7 ± 3.0	−7.9 ± 3.7		12
$Co(NH_3)_5Cl^{2+} + H_2O$	25	H_2O	−1.7 ± 1.0	−0.5 ± 1.2	+4.6 ± 0.7	13
first ionization of carbonic acid	25	H_2O	−15.0 ± 6.0	−11.9 ± 7.9	−14.8 ± 0.3	19

[a] Maleic anhydride.

themselves. This disection of activation volume implies that the first term in eq 21 is independent of pressure and the second term decreases with increasing pressure, because the main contribution to the former comes from changes in volume and shape of the relatively incompressible van der Waals spheres of the reactants, and the latter results from the restriction of thermal motions of solvated solvent molecules caused by strong solute–solvent interactions (an increase of internal pressure around polar solute molecules or ions).[21] Since the slope of a $\ln k_P - P$ plot decreases with pressure not only in heterolytic reactions but also in homolytic reactions, eq 21 would be better rewritten as follows:

$$\Delta V^\ddagger = \Delta V^\ddagger_{int} + \Delta V^\ddagger_{therm} \qquad (22)$$

where the second term is the change in the thermal volume that is created by thermal motions of reactants and solvent molecules and, therefore, it reaches zero at infinite pressure. As stated above, $\Delta V^\ddagger_{int}$ in eq 22 may be considered equal to $\Delta V_\infty^\ddagger$. The values of $\Delta V_\infty^\ddagger$ are listed in Table IX for several reactions with their standard deviations. Most of the values seem to be reasonable, judging from the reaction mechanisms, and they are in fairly good agreement with the $\Delta V^\ddagger_{int}$ values calculated by an independent method proposed by one of the present authors (eq 23).[8,21] In

$$-\frac{RT}{P-1}\ln\frac{k_P}{k_1} = \Delta V^\ddagger_{int} - \frac{\kappa}{P-1}\ln\frac{B+P}{B+1} \qquad (23)$$

eq 23, B is the Tait equation parameter of the solvent and $\Delta V^\ddagger_{int}$ and κ are the parameters to be adjusted. However, in some cases (hydrolyses of benzyl chloride and pentaamminechlorocobalt(III) ion), the agreement is poor and the $\Delta V_\infty^\ddagger$ values are rather unreasonable, probably because of the experimental errors and/or insufficient pressure range. Parameter a is relatively sensitive to the variation of $\ln (k_P/k_1)$ and to the selection of the data set in some cases. For example, in the hydrolysis of benzyl chloride, $\Delta V_\infty^\ddagger$ obtained by eq 10 becomes −1.2 ± 1.4 mL/mol when the data up to 5.5 kbar are used in the calculation. This fact indicates that accurate rate constants for wide pressure ranges are necessary in order to get a reliable and meaningful value for the parameter a. Although it is true that the measurements in relatively low pressure ranges suffice to get a reliable $\Delta V_0^\ddagger$, extending the pressure range will provide us further useful information for the understanding of reaction mechanisms.

Another Function To Describe Pressure Effects. If we restrict our purpose to the calculation of $\Delta V_0^\ddagger$, eq 24 seems to be the third

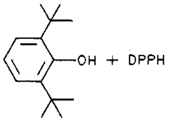
$$\ln\frac{k_P}{k_1} = aP + bP\ln(1 + cP) \qquad (24)$$

$$\frac{d\ln k_P}{dP} = a + b\ln(1 + cP) + \frac{bcP}{1 + cP} \qquad (25)$$

$$\Delta V_0^\ddagger = -aRT \qquad (26)$$

possibility.[22] This equation does not give a constant $\Delta V_\infty^\ddagger$ as can be seen in eq 25 but it is quite effective to describe experimental results. The $\Delta V_0^\ddagger$ and ss values for various reactions are given

TABLE X: Activation Volumes at Zero Pressure for Various Reactions Estimated by Eq 24

reaction	$\Delta V_0^\ddagger$, mL/mol	10^4(ss)
isomerization of NMe_2-NO_2-AB	−25.55 ± 0.30	1.898
$CH_2{=}C(Me)CH{=}CH_2$ + MA	−38.90 ± 1.19	22.81
$PhCH_2Cl + H_2O$	−8.81 ± 0.12	6.727
$Et_3N + EtI$	−28.42 ± 1.17	1.311
$TCNE + BuOCH{=}CH_2$	−47.30 ± 1.77	0.4478
	−14.99 ± 2.28	4.670
$Co(NH_3)_5Cl^{2+} + H_2O$	−18.37 ± 8.95	3.623
$Pt(dien)Br^+ + OH^-$	−25.16 ± 5.12	0.6066
ionization of H_2O at 25 °C	−21.32 ± 0.37	6.859
ionization of acetic acid at 25 °C	−11.58 ± 0.27	0.2141
first ionization of carbonic acid at 25 °C	−27.49 ± 0.25	0.6392
ionization of Et_3N at 30 °C	−52.10 ± 1.40	2.871

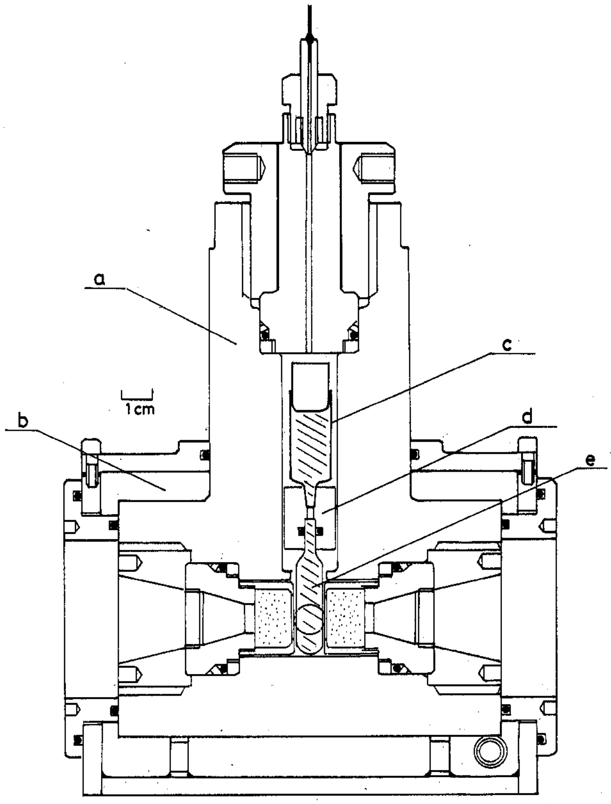


Figure 3. Optical pressure vessel: (a) pressure vessel; (b) water-circulating jacket; (c) hypodermic syringe; (d) Teflon coupler; (e) reaction solution.

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(21) Asano, T. *Rev. Phys. Chem. Jpn.* **1979**, *49*, 109.

in Table X. In the majority of the listed reactions, the ss value is the smallest for eq 24. However, the standard deviation for $\Delta V_0^\ddagger$ tends to be larger and in some cases it gives, probably unreasonably, large activation volumes. For example, in the aquation of $Co(NH_3)_5Cl^{2+}$, the average activation volume for 0.001 and P kbar changes as follows, −11.77 (0.5 kbar), −9.73 (1 kbar), −8.44 (1.5 kbar) mL/mol and the $\Delta V_0^\ddagger$ obtained by eq 24 is −18.37 mL/mol. The same tendency is observed in the hydrolysis of $Pt(dien)Br^+$ [−18.91 (0.125 kbar) mL/mol and $\Delta V_0^\ddagger = -25.16$ mL/mol]. These results indicate the difficulty in the estimation of $\Delta V_0^\ddagger$. This problem may be avoided if we choose to use $\Delta V^\ddagger$ under pressure, e.g., at 0.5 kbar, but it would result in another experimental difficulty, i.e., the partial molar volume measurements at high pressure in order to construct a volume profile of a reaction. Therefore, the most practical solution would be to use several equations in the estimation of $\Delta V_0^\ddagger$ and compare the obtained results.

Experimental Section

The rate constants for the Z–E isomerization of NMe_2-NO_2-AB were measured by the high-pressure flash spectroscopic technique described before.[8] The optical pressure vessel was slightly modified and its cross section is shown in Figure 3. The inner sample cell consists of a transparent glass cylinder and a hypodermic syringe and they are connected together with a Teflon coupler. Since the pressure is transmitted to the sample solution by means of the syringe, the possibility of a reduction in pressure by friction is eliminated. The pressure-transmitting fluid was hexane. The on-line calculations of the rate constants based on the Guggenheim method were performed by a SORD M200 Mark II computer. The least-squares calculations of the activation and reaction volumes were done by the Gauss–Newton method and/or by the Marquardt method. The program used was MULTI developed by Yamaoka.[23]

Registry No. (*Z*)-4-(Dimethylamino)-4′-nitroazobenzene, 73815-07-3.

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(22) We are grateful to one of the referees for the suggestion of this equation.

(23) Tanaka, Y.; Yamaoka, K. "Micro Computer Guide for Chemists"; Nankodo: Tokyo, 1981; pp 114–9.

Conformational Polymorphism. 5. Crystal Energetics of an Isomorphic System Including Disorder

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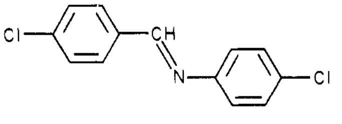
The methodology for investigating the influence of crystal forces on molecular conformation has been extended to an isomorphous system, involving chemically similar species which crystallize in essentially identical structures. The model systems chosen for this study are *p*-methyl-*N*-(*p*-chlorobenzylidene)aniline (CLME) and *p*-chloro-*N*-(*p*-methylbenzylidene)aniline (MECL), which crystallize in the monoclinic space group $P2_1/a$ with two molecules in the cell. Calculations involving the lattice energy minimization of the two structures were carried out to understand why the unstable planar conformation is stabilized by the lattice, although there are dimethyl- (MEME) and dichloro-substituted (CLCL) *N*-benzylideneanilines (BA) that contain lower energy molecular conformations. Furthermore, lattice energy calculations have been applied to hypothetical structures which are based on computationally substituting MEME and CLCL molecules into the CLME and MECL structures to determine whether it is possible that these analogues will pack as isomorphs of the system studied here, and to reveal the role of the substituents on disorder. Two different potential functions were applied (6–12 and 6-exp), both of them yielding lower energies for MECL than for the hypothetical structures and the lowest energies in comparison with minimized lattice energies of all BA compounds investigated to date. Analysis of the partitioned partial atomic energies was carried out to examine the similarities and differences in packing between the two isomorphs and the hypothetical structures. The relative stability of MECL arises from the favorable energetic environment of the ring, especially due to methyl and chlorine substituents.

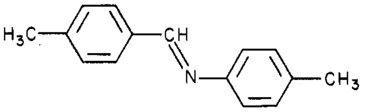
Introduction

A number of earlier studies[1-3] have demonstrated the utility of employing conformational polymorphism to investigate the role of crystal forces in influencing molecular conformation. The system employed in the first of those was the dimorphic *p*-chloro-*N*-(*p*-chlorobenzylidene)aniline (CLCL) which adopts different conformations in the two polymorphs.[4,5] The analysis of the energetics of CLCL[1] revealed a favorable energy for the triclinic structure, which accounts for the stabilization of the more highly energetic planar conformation in this form over the nonplanar one present in the orthorhombic polymorph.[6]



CLCL

In the second example[2] we asked why CLCL does not pack in a crystal in which the intramolecular energy is minimal. This was investigated computationally by substituting the CLCL molecule into the structure of form II of MEME in which the molecule



MEME

[†] In partial fulfillment of the requirements for the Ph.D. degree, Ben-Gurion University of the Negev.

(1) J. Bernstein and A. T. Hagler, *J. Am. Chem. Soc.*, **100**, 673 (1978).
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