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Effect of High Pressure on the Topography of Potential Energy Surfaces

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Abstract

Properties and reactivity of chemical compounds change dramatically at elevated pressures. Since kinetics and mechanisms of condensed-phase reactions are described in terms of their potential energy (PES) or Gibbs energy (GES) surfaces, chemical effects of high pressure can be assessed through analysis of pressure-induced deformations of GES of solvated reaction systems. We discuss general trends expected for such changes and use quantum mechanical calculation to construct PES of compressed species for hydrogen and methyl transfer reactions.

Keywords:

high pressure effects, volume profiles, reaction barriers, transition states, potential energy surfaces, Gibbs energy surfaces

1. Introduction

Since the early days of transition state theory, potential energy surfaces (PES) have been an indispensable tool for discussion of reaction mechanisms and dynamics at ambient pressures.¹ However, although PES accurately represent energetics of reaction systems in gas phase, free energy or Gibbs energy surfaces (GES), properly incorporating the solvation effects, are more adequate for similar purposes in the case of condensed phase reactions.² High pressures have a profound effect on reaction rates³ and may unveil completely new patterns of chemical reactivity when the strength of intermolecular interactions reaches the level of intramolecular forces.⁴ PES and GES naturally lend themselves as a powerful instrument for studying high pressures effects on reaction systems through analysis of the pressure-induced changes in their topography.^{5,6}

Although GES are more appropriate for discussion of high pressure effects on condensed phase reaction kinetics and mechanisms, high pressure PES (or, more precisely, enthalpy surfaces) offer a significantly cheaper alternative at sufficiently high levels of compression, when entropy effects are no longer essential.⁷ It has previously been demonstrated for the Diels-Alder dimerization of cyclopentadiene⁸ and hydrogen transfer between halogen atoms⁵ that under the extreme pressure conditions their energy landscapes undergo significant changes resulting in considerable reduction and, sometimes, complete elimination of reaction barriers. In the present work, we discuss general trends in pressure-induced changes to PES of compressed species, and report our findings for hydrogen transfer in hydrocarbon systems and methyl transfer in S_N2 processes in comparison with the results for simple triatomic X-H-Y systems (X,Y= F,Cl,Br).

Quantum-mechanical (QM) calculations were performed at the B3LYP/6-31++G(d,p) level using the Gaussian09 suite.⁹ Cavity images shown in Figures 3, 4, and 14 were produced using

the VMD package¹⁰ as graphic renderings of molecular dynamics (MD) trajectories generated using the GROMACS package.¹¹

2. General aspects of high pressure effects on the energy landscapes

If $\mathbf{x}_P$ is a position vector, describing a stationary point (reactant or product minimum, or a transition state (TS)) of a GES $G(\mathbf{x}; P)$ at pressure P , then

$$\frac{\partial G(\mathbf{x}_P; P)}{\partial x_i} = 0 \quad (1)$$

where x_i is an i -th component of vector $\mathbf{x}$. Eq. (1) defines $\mathbf{x}_P$ as an implicit function of P . If, as shown in Fig. 1 for a symmetric exchange reaction, coordinates $\mathbf{x}$ are chosen to be normal modes of $G(\mathbf{x}; P)$ at points $\mathbf{x}_P$, *i.e.* such that the cross-derivatives $\partial^2 G(\mathbf{x}_P; P) / \partial x_i \partial x_j$ ($i \neq j$) are zeros, the isothermal pressure derivative of $\mathbf{x}_P$ is

Insert Fig. 1 here

$$\left(\frac{(\partial \mathbf{x}_P)_i}{\partial P} \right)_T = - \left(\frac{\frac{\partial}{\partial P} \left(\frac{\partial G(\mathbf{x}_P; P)}{\partial x_i} \right)_T}{\frac{\partial^2 G(\mathbf{x}_P; P)}{\partial x_i^2}} \right) \quad (2)$$

And since volume V is an isothermal pressure derivative of Gibbs energy G , eq. (2) reduces to

$$\left(\frac{(\partial \mathbf{x}_P)_i}{\partial P} \right)_T = - \left(\frac{\frac{\partial V(\mathbf{x}_P; P)}{\partial x_i}}{\frac{\partial^2 G(\mathbf{x}_P; P)}{\partial x_i^2}} \right) \quad (3)$$

That is, the effect of pressure on the location of a stationary point should be stronger for softer modes (with lower values of the force constants $\partial^2 G / \partial x_i^2$). The direction of the shift (*i.e.* the sign of $(\partial \mathbf{x}_P)_i / \partial P$) depends on the sign of the force constant $\partial^2 G / \partial x_i^2$ and how the volume V of the reaction system depends on x_i .

Insert Figs. 2 and 3 here

For example, in the case of a symmetric Diels-Alder reaction, such as cycloaddition of ethane to butadiene, a schematic GES of which is shown Fig. 2, the reaction coordinate is a symmetric combination of distances R_1 and R_2 between interacting carbon atoms (the white diagonal in the figure); the other normal mode is the antisymmetric combination of R_1 and R_2 . The volume dependence on these coordinates, as can be seen from Fig. 3, is quite different: it is strong for the reaction coordinate (symmetric mode) and zero for the orthogonal direction (antisymmetric mode). In accordance with eq. (3), this results in a considerable pressure-induced deformation of the GES along the reaction coordinate, whereas the reaction path remains the same at all pressures. Since the second derivatives of G with respect to reaction coordinate have opposite signs for the reactant minimum and TS, they move towards each other as pressure increases; and since such derivative for the reactant minimum is the smallest, the shift in the position of it is strongest compared to other stationary points (TS and product minimum). At sufficiently high pressures, the reactant minimum reaches the TS and annihilates it, leaving the product minimum as the only remaining stationary point of the GES.

The situation is somewhat different in the case of symmetric exchange reactions, where the volume dependence on the reaction coordinate (the so-called volume profile¹²) is better described by a curve with a minimum corresponding to the TS of the GES (see Fig. 4). Due to that, for a TS, the derivative of volume with respect to the reaction coordinate is zero, and

according to eq. (3), TS is not expected to move along reaction coordinate when pressure increases. The reactant and product minima will move toward the TS, as was the case for the reactant minimum of a symmetric Diels-Alder reaction, and at sufficiently high pressures all the stationary points coalesce to give a single minimum located at the former position of the TS (see F-H-F and Cl-H-Cl reaction profiles in Fig. 5 and energy surfaces in Ref. 5).

Insert Figs. 4 and 5 here

In the case of asymmetric exchange reactions, the minimum of the volume profile is no longer located at the TS. As a result, although both endothermic and exothermic minima are shifted by pressure toward the TS, the latter does not remain static and moves toward the endothermic minimum. At sufficiently high pressures, this minimum annihilates the TS, leaving a shoulder at the point of annihilation (see F-H-Cl reaction profiles in Fig. 5 and energy surfaces in Ref. 5).

It is interesting to note that the calculated reaction profiles of Fig. 5 are reasonably well represented by a combination of two parabolic diabatic terms, which is consistent with the fact that hydrogen and alkyl transfer reactions obey the Marcus relationship.^{1f,13} The two-parabola model seems to offer an easy pictorial interpretation of the observed trends in the pressure dependencies of reaction profiles. As two parabolas are shifted by pressure toward each other, the reaction barrier roughly estimated by their crossing point gets smaller. The TS's of a symmetric XHX system remain exactly in the middle, between reactant and product minima, up to the moment when the two parabolas fully overlap and these two minima collapse into a single one, thus fully eliminating the TS and reaction barrier. The situation is somewhat different for asymmetric XHY systems, where the TS and reaction barrier disappear when the minimum of the "endothermic" parabola crosses the branch of the "exothermic" parabola, thus leaving the

exothermic minimum the only stable state on the PES, with the remainder of the “endothermic” parabola manifesting itself as a dissymmetric shoulder on the reaction profile.

3. High pressure PES for S_N2 XCH_3Y^- and hydrocarbon $R'HR''$ systems

To further explore the high pressure effects on the energy landscape of exchange reactions, we extended our earlier studies of XHY systems⁵ to the case of radical hydrogen transfer in hydrocarbon systems $R'-H-R''$ ($R', R'' = \text{Me, Et, } i\text{-Pr}$) and anionic $X-CH_3-Y^-$ systems ($X, Y = \text{CN, F, Cl, BR}$) modeling S_N2 reactions.¹⁴ As previously, the reaction systems were inserted coaxially within a linear chain of Ne atoms as shown in Fig. 6,¹⁸ and positions of the terminal Ne atoms were adjusted to attain the desired degree of compression, while the geometry of the rest of the system was optimized. The PES were then constructed by scanning X-C and C-Y distances, R_{XC} and R_{CY} , in XCH_3Y^- or C-H distances, $R_{R'H}$ and $R_{HR''}$ in $R'HR''$ with a step of 0.005 nm, with positions of the terminal Ne atoms held fixed and the rest of parameters of the system optimized. The force of the longitudinal compression exerted onto the system by the Ne matrix was calculated as a negative derivative $F = -dU(L)/dL$ of the optimized energy $U(L)$ with respect to distance L between terminal Ne atoms. We considered three levels of compression: 0.1, 0.5, and 1.0 hartree/nm, referred to as low, medium, and high (the compression of 0.1 hartree/nm is roughly equivalent to 100 kbar in the case of the F-H-F system⁵).

Insert Fig. 6 here

The parameters of the stationary points obtained for symmetric and asymmetric systems at different levels of compression are summarized in Tables 1-4. In all cases, pressure has a profound effect on the PES topography. With increasing pressure, the reactant and product

minima shift toward the TS, as predicted by eq. (3), and the reaction barriers get lower. At sufficiently high compressions, all systems collapse into a single minimum. Two typical scenarios are illustrated in Figs. 7-9 showing trends in symmetric ($\text{F-CH}_3\text{-F}^-$ and $\text{CH}_3\text{-H-CH}_3$) and asymmetric ($\text{F-CH}_3\text{-Cl}^-$) systems. PES for other systems are included in the Supplementary Material.

Insert Tables 1-4 and Figs. 7-9 here

At lower compressions, the reaction paths are fairly similar to the zero-pressure paths despite the notable shift of reactant and product minima along the reaction coordinate. However, as pressure increases and deformation of the PES becomes more significant, the reaction paths shift in the diagonal direction towards the lower left corner. This behavior is common for both symmetric and asymmetric systems, with one notable difference – whereas the single minimum of a highly compressed PES for a symmetric system appears as the limit of the TS sequence, for the asymmetric system it appears as the limit for the sequence of the exothermic minima, as discussed in the previous section.

The pressure dependencies of the reaction barriers for symmetric systems are shown in Fig. 10. Radical systems displayed a stronger pressure dependence than the anionic system, which could be traced to a lesser shift of the reactant minimum along the reaction coordinate in the latter, as predicted by eq. (3) for stiffer systems (see Fig. 11 where the energy profiles for the radical and anionic systems are compared at the bottom of their reactant wells). The activation energies $E_{\text{ABC}}(P)$ for asymmetric A-B-C systems ($\text{A}=\text{X}, \text{R}'$; $\text{B}=\text{H}, \text{CH}_3$; $\text{C}=\text{Y}, \text{R}''$) obeyed the Marcus relation¹³

$$E_{\text{ABC}} = \frac{E_{\text{ABA}} + E_{\text{CBC}}}{2} \left(1 + \frac{1}{2} \frac{E_{\text{ABC}} - E_{\text{CBA}}}{E_{\text{ABA}} + E_{\text{CBC}}} \right)^2 \quad (4)$$

as evidenced by the linear correlation of Fig. 12 between their values obtained by direct QM calculations and from eq. (4).

Insert Figs. 10-12 here

4. Alternative models

Our results unequivocally indicate that pressure can cause dramatic changes in the energy landscapes of compressed species, up to a complete elimination of reaction barriers, which is consistent with unusual chemical reactivity observed under extreme pressure conditions.^{4,19} The simple 1D compression model we used offers an easy and transparent way of achieving these extreme conditions at minimal cost. However, although the compression force can be evaluated quite accurately in this model, it is often hard to assess the corresponding pressure, unless the reaction system is simple enough to allow imbedding of the 1D model in a 3D matrix as shown in Fig. 13. In this case, the cross-section area to which the force is applied is known and pressure can be easily calculated.⁵ However, such imbedding quickly becomes problematic as complexity of a reaction system increases, and is hardly possible even for relatively simple $X-CH_3-Y^-$ and $R'-H-R''$ systems discussed in this work. An elegant approach proposed by Cammi and co-workers⁶ allows one to tackle this problem. It utilizes the formalism of polarizable solvent continuum,²⁰ adjusted to represent the effects of compressed medium, and is suitable for solutes of various levels of geometrical complexity. Yet, as with the original polarizable continuum model, this approach rests on the concept of a host solvent cavity, defined in terms of the scaled van der Waals radii of the solute atoms. MD simulations seem to offer a more realistic description of a solvent cavity and a more consistent definition of molecular volume.²¹ Shown in Figs. 3, 4, and 14, such cavities can be obtained by averaging over MD trajectories of the solvent

particles and reflect the pattern of avoidance by those particles of the part of space occupied by the solute. The size and shape of these cavities is sensitive to solute geometry, as well as to the type and strength of solvent-solute interactions and physical conditions (temperature and pressure).

Insert Figs. 13 and 14 here

Fig. 14 illustrates the parallelism between two compression models – a 1D matrix and an MD medium. Progressive compression of the solute system is achieved either by a reduction of the size of the 1D matrix L , or by a decrease of the solvent volume in NVT MD simulations or pressure increase in NPT MD simulations. If necessary, the cavity volumes obtained through MD simulations can be used to define the cavity size in the continuum model by Cammi and co-workers.⁶ Moreover, these volumes can be used directly to describe the pressure effects on the GES in terms of an approximate thermodynamic equation⁵

$$\mathbf{G}(\mathbf{x}; P) = \mathbf{G}_0(\mathbf{x}) + \int_{P_0}^P V(\mathbf{x}; p) dp \approx \mathbf{G}_0(\mathbf{x}) + (P - P_0)V(\mathbf{x})$$

where $\mathbf{G}_0(\mathbf{x})$ is the GES at the reference pressure $P = P_0$. Finally, MD simulations of solvation Gibbs energies $\mathbf{G}_s(\mathbf{x}; P)$, say by the means of thermodynamic integration,²² provide a direct connection between GES $\mathbf{G}(\mathbf{x}; P)$ and gas-phase PES $U_0(\mathbf{x})$:

$$\mathbf{G}(\mathbf{x}; P) = U_0(\mathbf{x}) + \mathbf{G}_s(\mathbf{x}; P)$$

These approaches have previously been compared and produced consistent results.⁵

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Supplementary Material

Compressed potential energy surfaces for all reaction systems; full citation for ref 9.

Draft

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18. It appears that in the case of collinear XHY exchange reactions the longitudinal compression of the reaction systems constitutes the dominant factor in the overall effect of the hydrostatic pressure, far exceeding the lateral compression in its importance. As a result, 1D and 3D medium matrices offered comparable models for the description of compression effects on the PES of XHY systems.⁵
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Fig. 1 Schematic GES for a symmetric exchange reaction $A+BC\rightarrow AB+C$ ($A=C$). R_{AB} and R_{BC} are the distances between A and B, and B and C, respectively. The yellow and green circles represent, correspondingly, the reactant/product minima and the TS. The white line is a minimum energy reaction path, the red lines are the normal modes along the reaction path, and the yellow lines are the normal modes orthogonal to the reaction path.

Fig. 2 (a)-(c) Schematic GES for a symmetric Diels-Alder reaction, with the level of compression increasing from (a) to (c). R_1 and R_2 are the distances between interacting carbons of a diene and dienophile. The yellow and green circles represent, correspondingly, the reactant/product minima and the TS. The white diagonal lines represent the minimum energy reaction path. (d) Free energy profiles along the reaction path.

Fig. 3 Pressure dependence of the volume of ethene+butadiene system on symmetric and antisymmetric combination of distances R_1 and R_2 between interacting carbon atoms, illustrated by the change in the shape and size of the solute cavity in response to their variation: (a) $R_1 = R_2 = 0.19$ nm; (b) $R_1 = R_2 = 0.21$ nm; (c) $R_1 = 0.19$ nm; $R_2 = 0.23$ nm. The images were created by an overlap of instantaneous positions of the solvent particles along an MD trajectory obtained for a frozen solute. Comparison of (b) and (a) indicates that the volume of the solute cavity changes dramatically when $R_1 + R_2$ is reduced while $R_1 - R_2$ remains zero; whereas switching from (b) to (c) shows that the volume of the solute cavity does not change despite a significant shape variation when $R_1 - R_2$ is increased while $R_1 + R_2$ remains constant.

Fig. 4 Volume dependence on the reaction coordinate (volume profile) for a symmetric exchange reaction $\text{XH} + \text{X} \rightarrow \text{X} + \text{HX}$. The minimum of the curve corresponds to the TS of the reaction.

Fig. 5 Reaction profiles for exchange reaction systems at different levels of compression. Red circles represent adiabatic QM energy profiles along scaled reaction coordinate;⁵ solid and dashed lines represent parabolic approximations for diabatic terms describing the reactant and product state, respectively.

Fig. 6 XCH_3X^- system in a 1D Ne matrix: X is green, C is cyan, H is white, Ne is red. Pressure exerted on the reaction system is generated by a compressed Ne chain with terminal atoms fixed at distance L .

Fig. 7 PES for F-CH₃-F⁻ system at ambient conditions (a), low compression (b), medium compression (c), and high compression (d). The corresponding TS positions (marked by symbols) shift in the diagonal direction with increasing pressure. The arrows project TS positions between lower and higher compression PES's. The contour spacing is 10 kJ/mol.

Fig. 8 PES for $\text{CH}_3\text{-H-CH}_3$ system at ambient conditions (a), low compression (b), medium compression (c), and high compression (d). The corresponding TS positions (marked by symbols) shift in the diagonal direction with increasing pressure. The arrows project TS positions between lower and higher compression PES's. At high compression the system collapses into a single minimum (pink hexagon). The contour spacing is 10 kJ/mol.

Fig. 9 PES for F-CH₃-Cl⁻ system at ambient conditions (a), low compression (b), medium compression (c), and high compression (d). The corresponding TS positions are marked by symbols. The arrows project TS positions between lower and higher compression PES's. At medium and high compression the TS has been annihilated and the system collapses into the endothermic minimum. The contour spacing is 10 kJ/mol.

Fig. 10 The dependence of the reaction barriers E_a on the strength of compression force F for symmetric exchange reaction systems: open circles – XHX, filled circles – XCH_3X^- , filled squares – $R'HR''$. The graphs for $CNCH_3CN^-$ and FHF are plotted with a reference to the secondary energy axis.

Fig. 11 Energy profiles at the bottom the reactant wells for FH-F (green), FH-F⁻ (red) and FCH₃-F⁻ (blue) systems. The horizontal axis is a scaled displacement from the equilibrium distance r_e .

Fig. 12 Correlation between reaction barriers E_{ABC} for A-B-C systems ($A=X,R'$; $B=H,CH_3$; $C=Y,R''$) obtained by direct QM calculations and from the Marcus relation: open circles – XHY ($X,Y=F,Cl,Br$), filled circles – XCH_3Y^- ($X,Y=F,Cl,Br$), filled squares – $R'HR''$ ($R',R''=Me,Et$), red – zero compression, purple – low compression, green – medium compression, blue – high compression.

Fig. 13 Linear X-H-X system in a 3D Ne matrix: X atoms are green, H atom is white, the Ne atoms of a 1D submatrix are red, and all other Ne atoms of the matrix are grey.

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Fig. 14 Two ways of modeling compression of a reaction system (exemplified here by an S_N2 system $F^- + CH_3F$): longitudinal compression by a 1D solvent matrix (red balls), and isotropic compression by a 3D solvent (shown here as an overlay of light grey solvent particles sampled along an MD trajectory): top – lower compression; bottom – higher compression.

Table 1. Parameters of the B3LYP/6-31++G(d,p) PES of symmetric X-CH₃-X⁻ systems (X = CN, F, Cl, Br) embedded in compressing Ne matrices. Parameters of the zero-compression gas-phase PES are also included for comparison.

System	Compression	Reactant		TS	
		R_{XC} , nm	R_{CX} , nm	R_{XC} , nm	Reaction barrier, kJ/mol
NC-CH ₃ -CN ⁻	Zero	0.150	0.300	0.210	167
	Low	0.150	0.295	0.205	159
	Medium	0.150	0.260	0.195	137
	High	0.100	0.240	0.185	121
F-CH ₃ -F ⁻	Zero	0.145	0.255	0.185	43
	Low	0.145	0.240	0.180	35
	Medium	0.145	0.215	0.180	25
	High	0.145	0.190	0.165	7
Cl-CH ₃ -Cl ⁻	Zero	0.185	0.320	0.235	37
	Low	0.185	0.295	0.235	33
	Medium	0.180	0.265	0.225	28
	High	0.180	0.240	0.205	20
Br-CH ₃ -Br ⁻	Zero	0.200	0.335	0.255	28
	Low	0.200	0.295	0.245	26
	Medium	0.200	0.270	0.230	18
	High	0.195	0.215	0.220	13

Table 2. Parameters of the B3LYP/6-31++G(d,p) PES of asymmetric X-CH₃-Y⁻ systems

(X, Y = NC, F, Cl, Br) embedded in compressing Ne matrices. Parameters of the zero-compression gas-phase PES are also included for comparison.

System	Compression	X-CH ₃ + Y		X + CH ₃ -Y		TS		Reaction barrier, kJ/mol	
		<i>R</i> _{XC} , nm	<i>R</i> _{CY} , nm	<i>R</i> _{XC} , nm	<i>R</i> _{CY} , nm	<i>R</i> _{XC} , nm	<i>R</i> _{CY} , nm	X-CH ₃ + Y	X + CH ₃ -Y
NC-CH ₃ -F ⁻	Zero	0.145	0.265	0.265	0.150	0.200	0.185	130	60
	Low	0.140	0.290	0.255	0.145	0.200	0.185	126	53
	Medium	0.140	0.255	0.230	0.145	0.200	0.175	121	30
	High	0.140	0.230	0.215	0.140	0.190	0.160	117	12
NC-CH ₃ -Cl ⁻	Zero	0.145	0.315	0.320	0.185	0.235	0.210	190	24
	Low	0.145	0.300	0.280	0.185	0.220	0.205	187	20
	Medium	0.140	0.275	0.240	0.185	0.215	0.200	179	7
	High	0.140	0.255	0.220	0.180	0.210	0.190	177	1
NC-CH ₃ -Br ⁻	Zero	0.145	0.345	0.305	0.200	0.240	0.225	204	13
	Low	0.145	0.300	0.280	0.200	0.235	0.225	198	18
	Medium	0.145	0.290	0.260	0.200	0.225	0.220	191	4
	High	0.14	0.265	single minimum				no reaction	
F-CH ₃ -Cl ⁻	Zero	0.14	0.33	0.245	0.19	0.215	0.21	109	2
	Low	0.14	0.305	0.24	0.19	0.215	0.195	100	1
	Medium	0.14	0.285	single minimum				no reaction	
	High	0.14	0.265	single minimum				no reaction	
F-CH ₃ -Br ⁻	Zero	0.145	0.315	single minimum				no reaction	
	Low	0.145	0.29	single minimum				no reaction	
	Medium	0.14	0.28	single minimum				no reaction	
	High	0.14	0.255	single minimum				no reaction	
Cl-CH ₃ -Br ⁻	Zero	0.185	0.34	0.305	0.205	0.24	0.245	46	20
	Low	0.185	0.31	0.295	0.2	0.235	0.245	40	17
	Medium	0.18	0.28	0.26	0.2	0.23	0.22	31	11
	High	0.175	0.26	0.24	0.195	0.205	0.215	27	9

Table 3. Parameters of the B3LYP/6-31++G(d,p) PES of symmetric R'HR' systems (R' = Me, Et, i-Pr) embedded in compressing Ne matrices. Parameters of the zero-compression gas-phase PES are also included for comparison.

System	Compression	Reactant		TS	
		$R_{R'H}$, nm	$R_{HR'}$, nm	$R_{R'H}$, nm	Reaction barrier, kJ/mol
Me-H-Me	Zero	no minimum		0.135	64
	Low	0.110	0.220	0.135	45
	Medium	0.110	0.165	0.130	9
	High	0.120	0.120	single minimum	no reaction
Et-H-Et	Zero	no minimum		0.135	68
	Low	0.110	0.225	0.135	50
	Medium	0.110	0.165	0.125	14
	High	0.125	0.125	single minimum	no reaction
i-Pr-H-i-Pr	Zero	no minimum		0.135	70
	Low	0.110	0.230	0.135	54
	Medium	0.110	0.170	0.130	17
	High	1.15	1.35	1.25	2

Table 4. Parameters of the B3LYP/6-31++G(d,p) PES of asymmetric Me-H-R'' systems (R'' = Et, i-Pr) embedded in compressing Ne matrices. Parameters of the zero-compression gas-phase PES are also included for comparison.

System	Compression	Me-H + R''		Me + CH ₃ -R''		TS		Reaction barrier, kJ/mol	
		R _{MeH} , nm	R _{HR''} , nm	R _{MeH} , nm	R _{HR''} , nm	R _{MeH} , nm	R _{HR''} , nm	Me-H + R''	Me + H-R''
Me-H-Et	Zero	no minimum		no minimum		0.135	0.130	77	58
	Low	0.105	0.260	0.225	0.105	0.135	0.130	64	32
	Medium	0.105	0.170	single minimum				no reaction	
	High	0.105	0.140	single minimum				no reaction	
Me-H-iPr	Zero	no minimum		no minimum		0.140	0.130	84	49
	Low	0.108	0.228	0.213	0.108	0.138	0.128	72	25
	Medium	0.108	0.178	single minimum				no reaction	
	High	0.108	0.153	single minimum				no reaction	