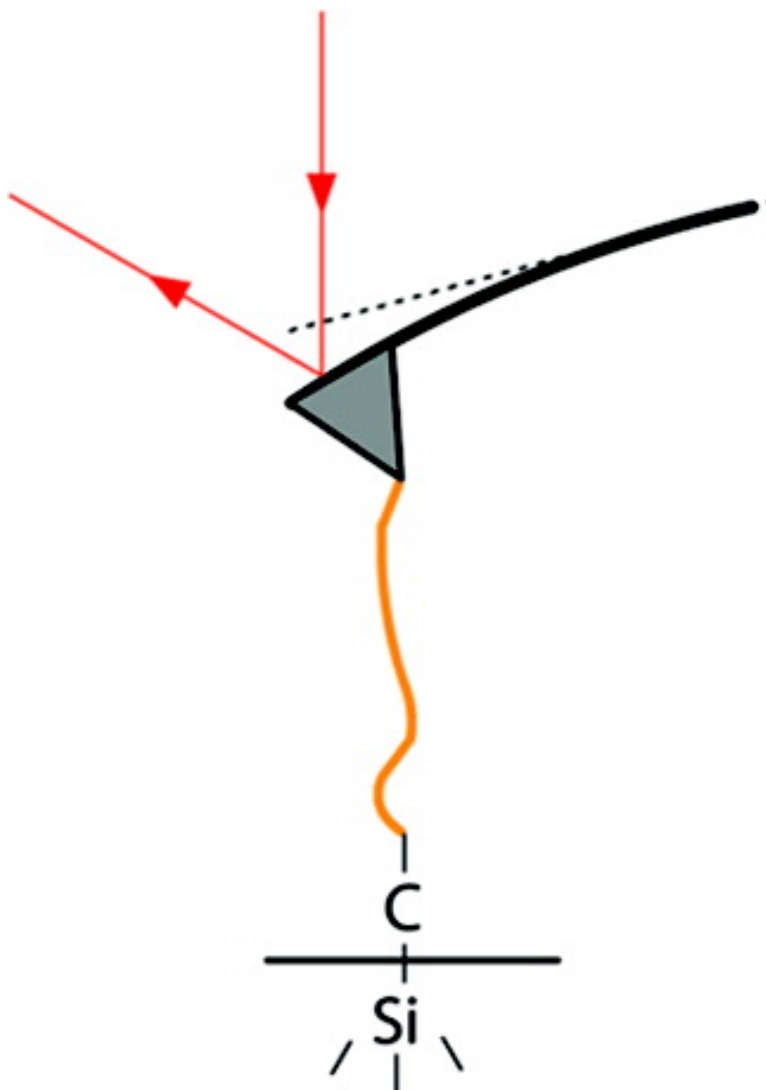


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Dynamic Strength of the Silicon–Carbon Bond Observed over Three Decades of Force-Loading Rates

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Abstract: The mechanical strength of individual Si–C bonds was determined as a function of the applied force-loading rate by dynamic single-molecule force spectroscopy, using an atomic force microscope. The applied force-loading rates ranged from 0.5 to 267 nN/s, spanning 3 orders of magnitude. As predicted by Arrhenius kinetics models, a logarithmic increase of the bond rupture force with increasing force-loading rate was observed, with average rupture forces ranging from 1.1 nN for 0.5 nN/s to 1.8 nN for 267 nN/s. Three different theoretical models, all based on Arrhenius kinetics and analytic forms of the binding potential, were used to analyze the experimental data and to extract the parameters f_{\max} and D_e of the binding potential, together with the Arrhenius A-factor. All three models well reproduced the experimental data, including statistical scattering; nevertheless, the three free parameters allow so much flexibility that they cannot be extracted unambiguously from the experimental data. Successful fits with a Morse potential were achieved with $f_{\max} = 2.0\text{--}4.8$ nN and $D_e = 76\text{--}87$ kJ/mol, with the Arrhenius A-factor covering $2.45 \times 10^{-10}\text{--}3 \times 10^{-5} \text{ s}^{-1}$, respectively. The Morse potential parameters and A-factor taken from gas-phase density functional calculations, on the other hand, did not reproduce the experimental forces and force-loading rate dependence.

Introduction

The fact that chemical reactions can be activated and controlled by mechanical force was recognized around 300 B.C. in Greece,¹ and today, the mechanical activation of chemical reactions through rubbing, grinding, milling, sonication, etc. is familiar to every chemist and chemical engineer.^{2–6} In a recent study, a team of chemists and material scientists from the University of Illinois at Urbana showed that tensile forces can even bias complex organic reaction pathways toward a desired direction by lowering activation energy barriers.⁷ In future applications, this may lead to more efficient chemical reactions as well as intelligent, stress-sensing or even self-healing materials. Furthermore, the fracture and rupture forces of macroscopic synthetic materials are directly related to the rupture

forces of chemical bonds,⁸ and for many practical applications, these forces are important design parameters.

With the advancement of single-molecule techniques, the mechanical properties of molecules and bonds have become experimentally accessible,^{9–13} and today, there are a number of experimental and theoretical studies dealing with the behavior of chemical bonds under tensile force.^{2,14–27} However, in all

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available experimental studies dealing with covalent bonds, the rate at which the force has been applied was kept constant, although it is generally believed that force-induced bond rupture is a thermally activated process, where the observed dissociation force depends on the force-loading rate, df/dt . Like in all thermally activated reactions, the reaction rate constant k^{off} is thought to be governed by an Arrhenius equation: $k^{\text{off}} = A \exp[-E_a/k_B T]$, where E_a is the height of the activation barrier, $k_B T$ represents the thermal energy, and the Arrhenius pre-factor A contains the activation entropy ΔS^\ddagger , the attempt frequency, and the transmission coefficient of the reaction.^{23,28}

To determine the height of the activation barrier in the case of force-induced bond separation, the potential energy stored in the force transducer, e.g., the loaded cantilever spring of an atomic force microscope (AFM), as well as in stretched spacer molecules has to be subtracted from the binding potential $V(x)$. For soft effective springs, like those typically used in single-molecule force spectroscopy, the potential energy stored in the deflected spring is approximately $f x$, where x is the direction of the applied force, which is assumed to coincide with the reaction coordinate. The effective binding potential can then be written as $V_{\text{eff}}(x) = V(x) - f(x - x_0)$, where x_0 is the location of the minimum of the original binding potential energy $V(x)$. The mechanical energy provided by the relaxing spring reduces the height of the activation barrier E_a , which in turn increases the reaction rate constant k^{off} . Thus, both the activation energy and the off-rate become force dependent and can be directly derived from the effective potential $V_{\text{eff}}(x)$. As a consequence, if the force is increased gradually, the observed bond rupture force f_r depends on the force-loading rate df/dt , and the functional relationship between f_r and df/dt contains structural information of the original binding potential $V(x)$ as well as the dissociation pathway.^{29,30}

Because researchers still lack data about the force-loading rate dependence of rupture forces of covalent bonds, in the present study, we have investigated the dynamic strength of the Si–C bond by systematically varying the applied force-loading rate over 3 orders of magnitude. We have employed AFM-based single-molecule force spectroscopy to stretch individual carboxymethylated amylose polymers, which have been covalently anchored between an amino-silanized glass surface and an amino-functionalized AFM tip, until the connection between the substrate surface and AFM tip was lost. As has been shown in previous studies,^{15,19} this rupture event can be attributed to the failure of the Si–C bond of the amino–silane surface anchor, which is the weakest bond in the molecular chain connecting the AFM tip and substrate surface. To extract the structural parameters of the binding potential, as well as kinetic information about the bond dissociation, we have compared the experimental results to Arrhenius kinetics models based on Morse and x^3 -binding potentials, and to structural data derived from first-principles quantum chemical calculations.

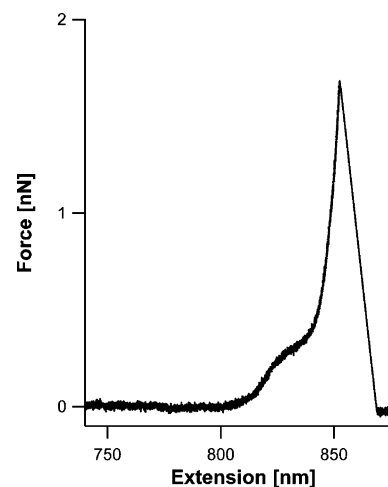


Figure 1. Force–extension curve of a single carboxymethylated amylose polymer in an atomic force microscope. Up to an extension of approximately 800 nm, the polymer uncoils. The bond angles then deform, and the chair–boat transition of the sugar rings leads to a pronounced plateau around 0.3 nN. Further extension of the molecule leads to a sharp force increase. At 1.69 nN, the Si–C bond in the surface linker of the molecule breaks, and the force drops to zero.

Results and Discussion

A typical force–extension curve of a covalently anchored carboxymethylated amylose polymer is shown in Figure 1. As has been shown in previous studies, the force curve exhibits a characteristic plateau, starting at around 0.3 nN, which has been attributed to a boat-to-chair conformational transition of the sugar rings of the polymer. During this conformational transition, the monomer length of carboxymethylated amylose increases by 0.5 nm.^{31–33} Because this plateau would appear at significantly higher forces, smear out, or disappear altogether if more than one molecule were stretched at a time, the plateau can be used to confirm that only a single polymer is stretched, and other force curves can be discarded. At the end of the plateau in Figure 1, the force increases rapidly. At a force of 1.69 nN, the connection between the AFM tip and substrate surface is lost, and the AFM cantilever spring relaxes to zero force. The force curve was recorded at a z -piezo velocity of 10 $\mu\text{m/s}$. Together with the slope of the force z -piezo–distance curve immediately before the connection is lost, this z -piezo velocity yields a force-loading rate of 109 nN/s. It should be mentioned that, because of the nonlinearity of the polymeric spacer, the assumption of a constant force-loading rate over the entire time scale of the experiment is, in fact, an approximation.^{24,34,35} However, for covalent bonds, the probability of a bond failure in the nonlinear low-force regime (below ~ 0.4 nN) is many orders of magnitude smaller than that at higher forces;¹⁹ therefore, force-dependent force-loading rates can be neglected.

As pointed out in the methods section (provided as Supporting Information), when approaching the substrate, the contact force between the AFM tip and substrate surface was kept below 0.3 nN, to avoid nonspecific attachment of sugar polymers to

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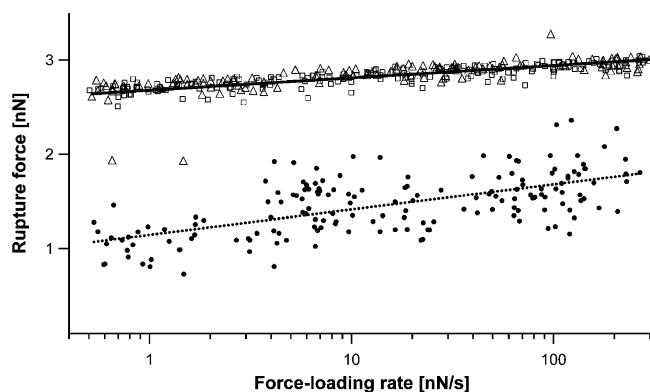


Figure 2. Scattered data plot of 165 Si–C bond ruptures (black dots). Here, each data point corresponds to a single rupture event, and the rupture force (vertical axis) is plotted versus the force-loading rate (horizontal axis). The dotted line shows a logarithmic fit to the experimental data (cf. also eq 1). The open squares and triangles represent two sets of simulated data, which were generated with an Arrhenius kinetics model with the parameters $A = 5 \times 10^{13} \text{ s}^{-1}$, $D_e = 337 \text{ kJ/mol}$, and $f_{\text{max}} = 4.8 \text{ nN}$, which were extracted from gas-phase DFT calculations of a stretched model molecule. The black line shows a logarithmic fit to the simulated data plots.

the AFM tip.^{15,33,36} Under these conditions, we were able to pick up molecules with the AFM tip in approximately 10–20% of all tip–substrate contacts. On the other hand, in control experiments, where the carboxymethylated amylose polymer was not activated, no molecules were picked up by the AFM tip at contact forces below 0.3 nN.

In Figure 2, the rupture forces of 165 bond ruptures are plotted against the applied force-loading rate in a semi-logarithmic representation (black dots). The force-loading rates span a range from 0.5 to 267 nN/s, the forces range from 0.7 to 2.36 nN, and the mean forces range from 1.1 to 1.8 nN. It should be noted that, in single-molecule force spectroscopy, the results are traditionally displayed in rupture force distributions (cf. also Supporting Information). However, the exact shape of the distributions and the position of their maxima strongly depend on arbitrarily chosen data ranges and bin widths. This can be avoided by displaying the experimental results in a scattered data plot, as in Figure 2.

The dotted line in Figure 2 represents a logarithmic fit to the data, where we used an Arrhenius kinetics model introduced by Evans and Ritchie.²⁹ According to this model, for binding potentials where the distance between the binding potential minimum and the transition state does not depend on the applied force, the most probable bond rupture force f_{mp} should increase logarithmically with the applied force-loading rate:

$$f_{\text{mp}} = k_{\text{B}}T/\Delta x^{\ddagger} \ln[(df/dt) \Delta x^{\ddagger}/(k_0^{\text{off}} k_{\text{B}}T)] \quad (1)$$

Here, Δx^{\ddagger} is the distance between the potential minimum and the transition state, and k_0^{off} is the off-rate at zero force. The free parameters in this model are Δx^{\ddagger} and k_0^{off} , and the fit yields values of 0.35 Å and $3.85 \times 10^{-4} \text{ s}^{-1}$, respectively. However, although the logarithmic increase of rupture forces with increasing force-loading rate seems to model our data quite well, comparing the values of the fit parameters to typical bond lengths and lifetimes $\tau_0 = 1/k_0^{\text{off}}$ of covalent bonds¹⁹ shows that especially the bond lifetime is significantly underestimated by

this widely used model. To understand why covalent bonds are not adequately represented by this model, one has to keep in mind that, for binding potentials without a sharp activation barrier, like a Morse potential, the assumption that Δx^{\ddagger} is constant is no longer valid, because the distance between the potential minimum and the transition state becomes a function of force.

To model the experimental data more accurately and extract kinetic and structural information about the bond rupture process and the binding potential, we simulated scattered data plots using an Arrhenius kinetics model, where a Morse potential was chosen as a one-dimensional representation of the covalent bond:

$$V(x) = D_e[1 - \exp(-\beta x)]^2 \quad (2)$$

$$\beta = 2f_{\text{max}}/D_e$$

The maximum force f_{max} — i.e., the slope at the inflection point of the potential — and the bond dissociation energy D_e may be extracted from density functional theory (DFT) calculations of a stretched model molecule, or they can be chosen as fit parameters in an effort to model the experimental results.

The effective potential $V_{\text{eff}}(x) = D_e[1 - \exp(-\beta x)]^2 - fx$, together with a suitably chosen Arrhenius pre-factor, allows for an analytic calculation of the Arrhenius rate of bond dissociation as a function of force, which can be converted into a bond rupture probability within a given force interval at a given force-loading rate. This probability can, in turn, be used to generate simulations of experimental results with a random number generator. For a detailed description of the Arrhenius kinetics model, refer to refs 19, 23, and 37. The open squares and triangles in Figure 2 show two sets of a simulated scatterplot. The parameters $f_{\text{max}} = 4.8 \text{ nN}$, $D_e = 337 \text{ kJ/mol}$, and a load-dependent A -factor covering the range $1 \times 10^{13} - 5 \times 10^{13} \text{ s}^{-1}$ for the Si–C bond were directly taken from previously published DFT calculations in the gas phase.¹⁹ In this case, the Arrhenius pre-factor corresponds to the maximum optical phonon frequency of the polymer. However, as noted previously,^{2,15,19} these gas-phase calculations do not quantitatively reproduce the measured rupture forces: The simulated rupture forces lie well above the experimental data, and the loading rate dependence is less pronounced in the simulation, as evidenced by the logarithmic fit (black line in Figure 2). The fact that the modeled rupture forces are above the experimental values has been attributed to the absence of solvent effects, which are likely to lower the bond dissociation energy but also weaken the maximum force.^{15,23,24}

Moreover, the optical phonon frequency merely constitutes an upper limit of the Arrhenius pre-factor, which can be expressed as $A = \kappa \nu q^{\ddagger}/q$, where κ is the accommodation coefficient, ν the attempt frequency, and q^{\ddagger}/q the ratio of the partition functions of the activated complex and the initial state, respectively. As has been pointed out,²³ for reactions in liquid, the accommodation coefficient is usually smaller than 1, the attempt frequency may be significantly reduced by solvation and viscous drag, and the ratio of the partition functions, which is proportional to $\exp(\Delta S^{\ddagger}/k_{\text{B}})$, is usually smaller than 1, due to conformational constraints of the activated complex.^{23,28} Con-

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Table 1. Free Parameters of Simulated Scattered Data Plots^a

scale factor $A_{\text{opt}} = 5 \times 10^{13} \text{ s}^{-1}$	D_e (kJ/mol)	f_{max} (nN)	$1/\beta$ (Å)
1	120.5	8.1	0.12
10^{-2}	99.2	6.2	0.13
10^{-4}	87.6	5.1	0.14
3×10^{-5}	86.5	4.8	0.15
10^{-6}	75.0	4.3	0.14
10^{-8}	68.9	3.0	0.19
10^{-9}	70.3	2.3	0.25
2.45×10^{-10}	75.8	2.0	0.31
10^{-10}	67.5	1.9	0.29
10^{-11}	48.2	1.7	0.24

^a The force-dependent optical phonon frequency in the Morse potential-based Arrhenius kinetics model¹⁹ was scaled by a fit parameter.

sequently, for reactions in a liquid environment, the A -factor is expected to be much smaller than the optical phonon frequency in a vacuum.

As discussed above, the decrease in bond dissociation energy may be rationalized with the solvation energy of the fragment radicals. Alternative mechanisms could involve the attack of a stretched bond by protons or other ions from the solvent,^{20,38} or even a mechanically activated chemical reaction^{2,7,39} of the mechanoradicals with the linker chemicals, which are used to activate the carboxyl groups and which might still be present in the reaction medium in small quantities. If the mechanically activated bond is attacked by one of those molecules, the chemical reaction may even precede the homolytic bond cleavage. The D_e value derived from the fit is, in this case, the activation energy of a mechanically activated polymerization. The attack of the diffusing reactant molecule would widen the potential and lower the maximum force. Since the diffusion of a second reactant into the correct position is involved, this would also account for a significant lowering of the Arrhenius A -factor relative to the gas-phase values.

It is interesting to test whether the scatter plot simulation with the Morse potential Arrhenius kinetics model is, in principle, able to reproduce the rupture forces, the load dependence, and the statistical scattering of the experimental data points. Therefore, we have systematically varied the two parameters f_{max} and D_e of the Morse potential and scaled the Arrhenius A -factor in the one-dimensional model polymer until we obtained simulated data sets which closely resembled the experimental results. Table 1 summarizes the fit parameters obtained in this way.

The parameters span a wide range because we have stretched the boundaries of all three parameters. The physically most reasonable parameters are between the lines printed in bold, which mark the upper and lower limits of the rupture force. The upper limit of the rupture force is given by $f_{\text{max}} = 4.8$ nN, calculated in the gas phase by DFT. Higher values of f_{max} would indicate that a different bond might be breaking, which seems unlikely because the previously published mirco-ruptures,¹⁵ which can also be observed in our data, point to a bond present only in the surface anchor of the molecule, and here all other bonds should be significantly stronger than the Si–C bond.¹⁹ The lower limit of $f_{\text{max}} = 2$ nN is given by the upper limit of the experimentally observed ruptures, if one regards the two data points around 2.3 nN as statistical scattering. Note that

$1/\beta$, which is proportional to the width of the Morse potential (cf. eq 2), reaches a maximum at $f_{\text{max}} = 2$ nN, with $1/\beta = 0.31$ Å. The gas-phase value, on the other hand, is 0.58 Å. This might be an indication that f_{max} is actually reached at 2 nN, assuming that the width of the potential is less affected by the solvent than the other parameters. However, with the present data, this remains speculation, and further experiments at higher force-loading rates are required to clarify this point. It should also be noted that, for the wide range of $f_{\text{max}} = 2.0$ –4.8 nN, the corresponding bond energies amount to $D_e = 75.8$ –86.5 kJ/mol, spanning a comparatively narrow range. At the same time, the Arrhenius A -factor varies over 5 orders of magnitude.

Interestingly, fitting our data with an analytical model for a Morse potential under tension, which has recently been introduced by Hanke and Kreuzer,²³ gives nearly the same result. According to this model, the most probable bond rupture force f_{mp} at a certain force-loading rate is given by

$$1 - 2 \frac{f_{\text{mp}}}{\beta D_e} = \frac{\beta A k_B T}{4(df/dt)} \exp \left[- \frac{D_e}{k_B T} \left(1 - 2 \frac{f_{\text{mp}}}{\beta D_e} \right)^2 \right] \quad (3)$$

Here, A is the Arrhenius pre-factor, and β and D_e represent the width and the depth of the Morse potential, as defined in eq 2. The possible fit parameters again span a wide range, and they closely resemble the values of the simulated scatter plots of Table 1 (cf. also Supporting Information). It should be noted, however, that it was not possible to fit our data with three free parameters. Instead, we had to set one parameter — here f_{max} — to a reasonable predetermined value and treat the other two as free parameters. With this model, an unambiguous determination of all three free parameters is again not possible.

Figure 3A displays the overlap of the experimental data (black circles) with the simulated scattered values (open squares and triangles) for $A \approx 1.5 \times 10^9 \text{ s}^{-1}$ (scale factor 3×10^{-5}), $D_e = 86.5$ kJ/mol, and $f_{\text{max}} = 4.8$ nN. As can be seen from the virtually indistinguishable logarithmic fits (black solid line), the agreement between experiment and simulation is quite good. The red line in Figure 3A shows a fit of the analytical model by Hanke et al. for $f_{\text{max}} = 4.8$ nN, and the fit parameters $A = 2 \times 10^8 \text{ s}^{-1}$ (scale factor 4×10^{-6}) and $D_e = 73.1$ kJ/mol. Again, the agreement with the experimental data is quite good. Figure 3B shows the same experimental data together with simulations, but now the simulated values span an experimentally inaccessible range of force-loading rates of 21 decades. The solid line in Figure 3B shows again the analytical model by Hanke and Kreuzer.²³

As predicted by those authors, the distribution reaches a maximum when the rupture force reaches f_{max} , in this case at 4.8 nN. At small force-loading rates, however, the Hanke and Kreuzer model reaches zero force much faster than in our simulated scatter plot: The analytical model predicts vanishing bond rupture force for force-loading rates around 10^{-6} nN/s, whereas the simulated scatter plot approaches zero at force-loading rates below 10^{-8} nN/s.

Finally, it should be mentioned that an alternative analytical model, introduced by Dudko et al.,⁴⁰ who proposed approximating the Morse potential under tension by an x^3 -binding potential, could also be used to fit our experimental data. Yet, this model did also not furnish unique fit parameters. Moreover, as pointed

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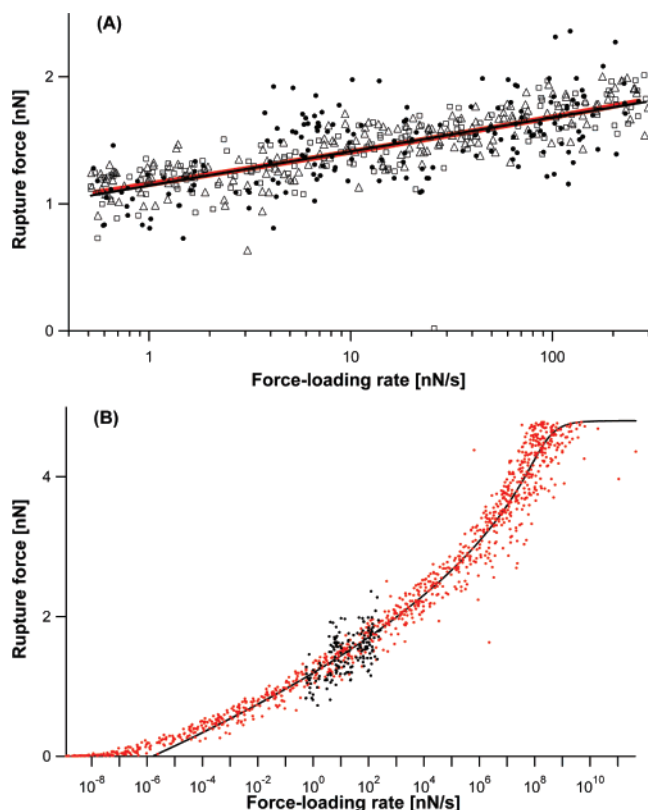


Figure 3. (A) Comparison of experimental (black dots) and simulated scattered data plots (open squares and triangles). For the simulated data, the parameters of the Arrhenius kinetics model were treated as free parameters, in an attempt to fit the model to the experimental data. The parameters used to generate the simulated data are $A \approx 1.5 \times 10^9 \text{ s}^{-1}$, $D_e = 86.5 \text{ kJ/mol}$, and $f_{\text{max}} = 4.8 \text{ nN}$, which is one of several possible sets of parameters that yield good agreement with the experimental data (cf. also Table 1). The black line is a logarithmic fit to the experimental and the simulated data (because of the good agreement, the two fits are indistinguishable in the graph). The red line is a fit of eq 3 to the experimental data (fit parameters: $A = 2 \times 10^8 \text{ s}^{-1}$, $D_e = 73.1 \text{ kJ/mol}$, and $f_{\text{max}} = 4.8 \text{ nN}$). (B) The same data set as in panel A, but now the simulations and the fit of eq 3 span a range of 21 decades. Black dots represent experimental data, red dots simulated data, and the black line the fit of eq 3.

out by Dudko et al., the high force regime, where f_r is expected to approach f_{max} , is not accurately represented by this model.

Conclusion

We have investigated the force-loading rate dependence of the rupture force of the Si–C bond by variation of the force-loading rate over 3 orders of magnitude. As predicted by Arrhenius kinetics models, we found a logarithmic increase in bond rupture force as a function of the applied force-loading rate over the experimentally covered range. This clearly demonstrates that the force-induced dissociation of covalent bonds follows Arrhenius kinetics and that the observed bond rupture force is directly related to the bond lifetime.

However, our data also clearly indicate that, if an Arrhenius model with structural parameters extracted from gas-phase quantum chemical calculations is used, the model overestimates the bond rupture forces and underestimates the force-loading rate dependence. Therefore, these parameters have to be treated as free parameters, and their values have to be extracted from the experimental data. However, because with all three Arrhenius models used it is not possible to unambiguously extract all three free parameters, more experimental data spanning an even wider force-loading range and modifying additional experimental parameters, like temperature, are required.

Hanke and Kreuzer²³ have pointed out that, if it were possible to determine f_{max} independently from experiments with high force-loading rates, it would be much easier to derive the remaining two parameters from experimental data. Especially fast experiments with stiffer cantilever springs might allow investigators to actually reach f_{max} experimentally. Moreover, following the strategy of Wiita et al.,²⁵ probing the bond lifetime at constant force, rather than measuring bond rupture forces as a function of force-loading rate, might be an alternative to further spanning the force-loading range. However, as pointed out above, force-induced bond rupture is a thermally activated process, and its kinetics is controlled to a large extent by the ratio of activation energy E_a to thermal energy $k_B T$, which enters the exponent of the Arrhenius equation. For this reason, gathering temperature-dependent data should allow the free parameters of the Arrhenius model to be determined more accurately. Because the exponent of the Arrhenius equation is temperature dependent and the entropic term which enters the Arrhenius pre-factor does not depend on temperature, temperature-dependent measurements might be a versatile strategy to separate the activation energy E_a and the activation entropy ΔS^\ddagger and determine D_e and A independently.

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Supporting Information Available: Details of the experimental procedures, experimental rupture force distributions, as well as the fit parameters following the procedure by Hanke and Kreuzer²³ and tables with the rupture force vs loading rate values of Figure 2. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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