13694 J. Phys. Chem. A **2009,** *113,* 13694–13699

A Semiempirical Capture Model for Fast Neutral Reactions at Low Temperature

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Received: June 15, 2009; Revised Manuscript Received: October 13, 2009

The description of Titan's chemistry relies strongly on reaction rate data collected at room temperature or above. However, the temperature in the atmosphere of Titan ranges from 70 to 200 K. We describe here a simple theoretical method to extend the available measurements toward those temperatures. It is based on the long-range capture theory combined with room temperature data. First results are presented for 28 neutral reactions involving atomic carbon, CN, CH, and C_2H radicals and are compared to low-temperature Cinétique de Réaction en Ecoulement Supersonique Uniforme measurements. A good agreement is observed, to within a factor of 2, for most reactions in the temperature range 13−295 K. Predictions are made for reactions of the CN radical with hydrocarbons and nitriles of particular importance in Titan's atmosphere.

Introduction

The exotic world of Titan, Saturn's largest moon, has emerged as a natural laboratory on a planetary scale to shed light on chemical evolution. Titan is the only Solar System solid body besides Earth and Venus with a thick atmosphere (1.5 bar at the surface). The temperature ranges from about 200 K in the upper atmosphere to 70 K at the tropopause.[1] The atmospheric composition consists of molecular nitrogen (N_2, 98%), methane (CH_4, 2%), as well as their photochemical progeny, which culminates in organic, brownish haze layers.[2,3]

Despite the crucial role of the haze layers in Titan's astrochemical evolution, radiation balance, and weather system ("antigreenhouse gases"),[4] the underlying chemical processes, which direct the haze formation, have been the least understood to date.[5] Photochemical atmospheric models concur that solar ultraviolet photons and energetic electrons from Saturn's magnetosphere processing the nitrogen and methane initiate Titan's chemistry. This processing links simple molecules such as nitriles via hydrocarbon species to the orange-brownish haze layers surrounding Titan.[6,7] The transformation of simple molecules into haze is the most fundamental step in the context of the evolution of hydrocarbon-rich planetary and satellite atmospheres in the Solar System.[5] For an understanding of the origin and evolution of Titan's haze layers, it is imperative to elucidate the synthetic routes to the "missing link" between simple gas-phase molecules and complex species, i.e., the simplest building block coupling Titan's hydrocarbon and nitrogen chemistries. Understanding the macroscopic evolution of Titan's atmosphere requires the knowledge of the detailed microscopic mechanism involving multiple elementary bimolecular encounters between molecules.

Here, we report on a semiempirical theory to extend neutral−neutral rate constants from room temperature down to very low temperatures ($T \approx 10$ K). Our method is based on the application of the capture theory[8] at very low temperature combined with room temperature data. The method is described in section 2, and first results are presented in section 3 for reactions involving atomic carbon, CN, CH, and C_2H radicals. Our conclusions are drawn in section 4.

Model

A large number of neutral−neutral reactions involving radicals have been experimentally shown to remain rapid down to temperatures as low as 13 K (see the review by Smith[9] and references therein). Moreover, the rate constants generally increase as the temperature is lowered, in disagreement with both the Arrhenius equation and, to a lesser extent, with long-range capture theory. A number of theoretical treatments have been proposed to explain this temperature dependence. A convincing explanation has been provided by the so-called two transition state model which was successfully applied, in particular, to reactions of oxygen atoms with alkenes (Sabbah et al.[10] and references therein). This model is based on the existence of a "submerged" potential energy barrier along the minimum energy path from reactants to products.[11] This barrier, which is difficult to predict reliably, provides a second "inner" transition state that controls the reaction rate at relatively high temperatures. At extremely low temperatures, however, the reaction rate is controlled by the "outer" capture transition state. Dynamical effects subsequent to capture have also been investigated by Faure et al.[12] using a parametric atom−diatom potential and quasi-classical trajectories. This study has shown that a submerged barrier in the entrance reaction valley induces strong vector correlations between partial angular momenta. In particular, a strong decrease of the rate constant with increasing rotation of the diatom (i.e., temperature) was obtained. It should be noted that the inhibition of reactivity with increasing rotational angular momentum was established experimentally long ago for ion−molecule reactions (see, e.g., Gerlich and Rox[13]), but it was observed only recently for neutral systems (see Olkhov and Smith[14] and references therein). We note finally that spin−orbit effects were also shown to account for the negative temperature dependence of fast reactions, in particular those involving open-shell atoms such as Si(^{3}P).[15]

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10.1021/jp905609x CCC: $40.75

Concerning the modeling of Titan's and interstellar chemistry, the major result of the low-temperature measurements is that the rates of fast neutral reactions amount to a few times 10^{-10} cm^3 s^{-1} at very low temperature ($T < 50$ K), that is are close to the capture limit and are only an order of magnitude below typical rates for ion−molecule reactions. We propose in this work a semiempirical approach to estimate the rate of fast reactions over the range 5−295 K, provided the room temperature value is known (experimentally or theoretically). Indeed, the rate constants generally follow power laws below room temperature and generally show a maximum between 10 and 50 K (see below). Hence the two crucial points here are (i) to predict which reactions remain fast at low temperature and (ii) if so, to estimate the capture value at low temperature. Concerning the first point, Smith[16] has shown from a careful examination of the experimental data collected up to 2006 that a radical-molecule reaction is likely to be rapid if its room temperature rate is greater than $\sim 10^{-11}$ cm^3 s^{-1} and its activation energy at 295 K is zero or negative. We note that Smith et al.[17] have also correlated the rate constants of fast neutral−neutral reactions with differences between the ionization energies of the molecular reagent and the electron affinity of the radical (see also Sabbah et al.[10]). Concerning the second point, Faure et al.[18] have found that the isotropic dispersion contribution to the long-range potential is dominant down to temperatures of a few kelvins. At lower temperatures, the electrostatic potential (e.g., dipole−dipole) becomes dominant, as also shown by Stoecklin et al.[19]

On the basis of the previous considerations, we suggest the following semiempirical model to extend the rate constant of a fast (exothermic) radical-molecule reaction from room temperature down to 5−10 K:

- At room temperature ($T_3 \approx 300$ K), the (experimental or theoretical) rate constant must be greater than 10^{-11} cm^3 s^{-1}. (Otherwise the reaction is expected to be negligible.)
- At T_1 and T_2 (both lying between 5 and 50 K), the rate constant is calculated from the capture theory by considering the (isotropic) dispersion interaction only, that is, by neglecting the electrostatic potential. The expression for the capture rate constant can be found for example in Stoecklin et al.[19]

$$k(T) = 2\sqrt{\frac{2\pi}{\mu}}\Gamma\left(\frac{2}{3}\right)(2C_6)^{1/3}(k_bT)^{1/6} \tag{1}$$

where μ is the reduced mass, k_b is the Boltzmann constant, $\Gamma(x)$ the gamma function, and C_6 is the dispersion coefficient. A well-known approximation for this coefficient is provided by the London formula:[20]

$$C_6^{\mathrm{London}} = \frac{3}{2}\frac{I_1I_2}{I_1 + I_2}\alpha_1\alpha_2 \tag{2}$$

where I_1 and I_2 are the ionization potentials and α_1 and α_2 the polarizabilities of the reactants, respectively. It has been shown empirically and from ab initio calculations, however, that eq 2 underestimates the dispersion magnitude by a factor of ~2 (see Faure et al.[21] and references therein). As a result, we have employed in eq 1 the following C_6 coefficient

$$C_6 = 2 \times C_6^{\mathrm{London}} \tag{3}$$

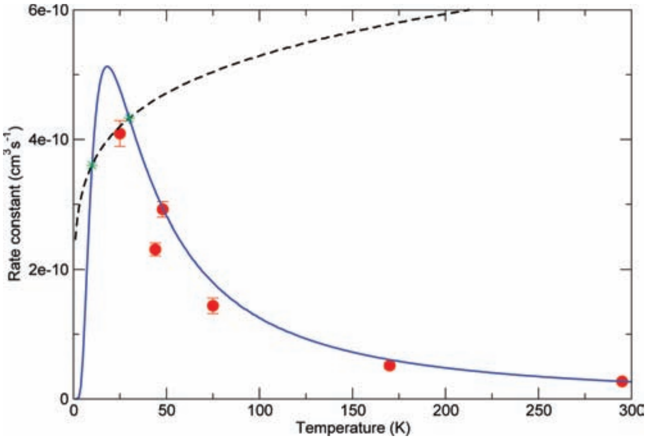

Figure 1. The rate constant of the reaction CN + NH_3 as a function of temperature. The capture prediction, eq 1, is given by the dashed line and stars denote values at 10 and 30 K. The data from the CRESU experiment is represented by the filled circles. The present model is denoted by the solid line.

It should be noted that the capture rate constant, eq 1, depends on $(C_6)^{1/3}$ only and a very accurate value for the dispersion term is not crucial.

The room temperature rate (k_3) and the capture rates (k_1 and k_2) are analytically interpolated by the standard 3-parameters equation

$$k(T) = \alpha(T/300)^{\beta}\exp(-\gamma/T) \tag{4}$$

which is routinely employed in astrochemical models for two-body reactions (see, e.g., Woodall et al.[22]). The expressions for α, β, and γ as functions of k_1, k_2, and k_3 are given in the Appendix. It should be noted, in particular, that β and γ are here linearly dependent.

We stress that the above "capture" temperatures, T_1 and T_2, can be adjusted as free parameters for a given radical species, as shown below. Finally, in the following, ionization potentials and polarizabilities were taken from Lide[23] except specified otherwise.

Results and Discussion

Comparisons to Results from Cinétique de Réaction en Ecoulement Supersonique Uniforme (CRESU) Experiments. A first application of the above model is presented in Figure 1 for the CN($X^2\Sigma^+$) + NH_3 reaction, which involves two strongly polar species. This reaction was found to show the strongest negative temperature dependence of any neutral−neutral system yet studied by the CRESU experiment.[24] It is employed here as a benchmark for our model. We observe in Figure 1 that the capture theory does not account for the negative temperature dependence of the experimental rate, as expected (see eq 1). The present semiempirical model, however, provides a fairly good qualitative description of the CN + NH_3 rate constant over the temperature range 25−295 K: the agreement is within 40% of the CRESU data. It should be noted that we have employed the capture temperatures $T_1 = 10$ K and $T_2 = 30$ K, which were found to provide the best results. The maximum at ~20 K therefore reflects the particular choice of both the capture temperatures and the form of eq 4. This artificial maximum is forced, by construction, to lie between 10 and 30 K. It is also too sharp owing to the exponential decrease of the rate below 20 K. A very low temperature maximum in the CN + NH_3 rate

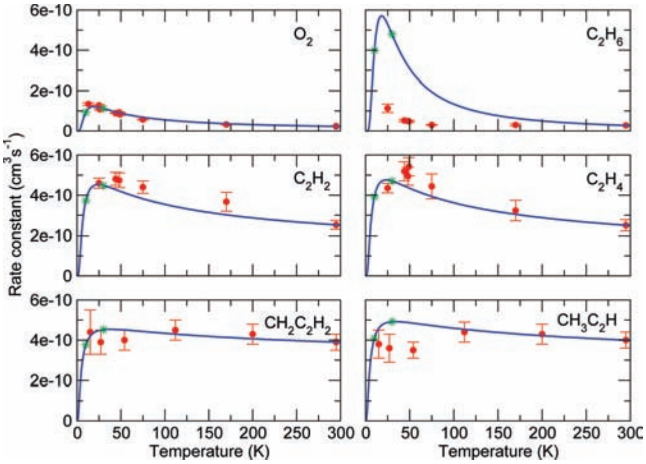

Figure 2. Same as Figure 1 for the CN radical reacting with O_2, C_2H_6, C_2H_2, C_2H_4, $CH_2C_2H_2$, and CH_3C_2H. See text for details and references.

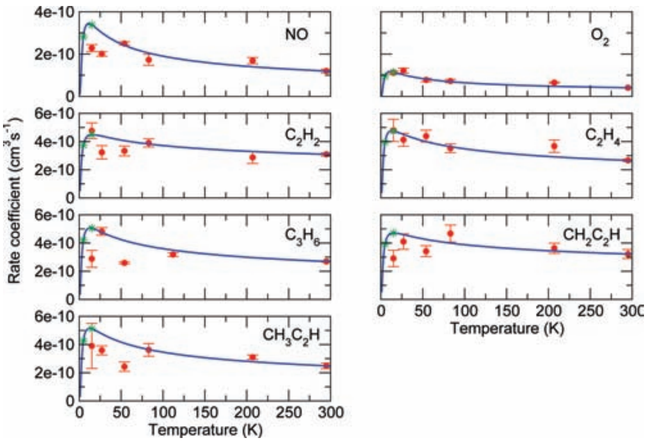

Figure 3. Same as Figure 1 for atomic carbon, $C(^3P)$, reacting with NO, O_2, C_2H_2, C_2H_4, C_3H_6, $CH_2C_2H_2$, and CH_3C_2 H. Stars denote capture values at 5 and 15 K. See text for details and references.

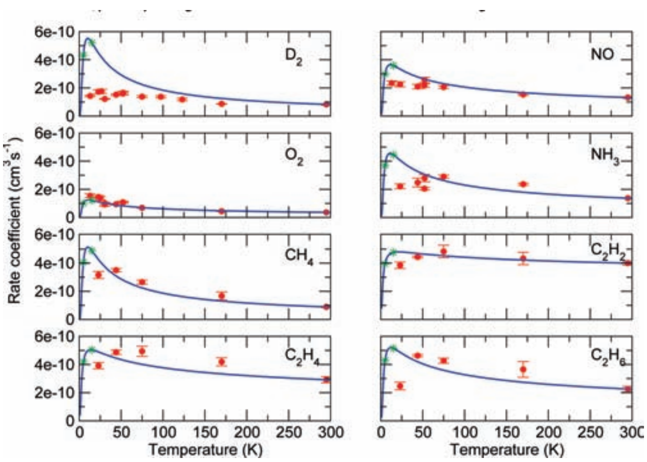

Figure 4. Same as Figure 3 for the CH radical reacting with D_2, NO, O_2, NH_3, CH_4, C_2H_2, C_2H_4, and C_2H_6. See text for details and references.

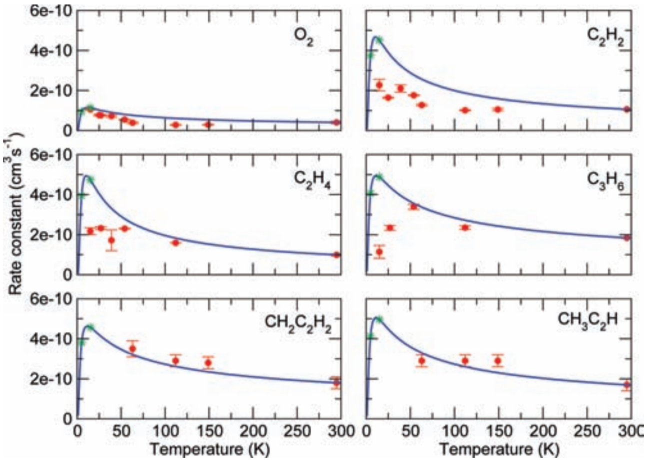

Figure 5. Same as Figure 3 for the C_2H radical reacting with O_2, C_2H_2, C_2H_4, C_3H_6, $CH_2C_2H_2$, and CH_3C_2 H. See text for details and references.

constant was actually predicted by the capture calculations of Stoecklin and Clary.[25] In their treatment, in addition to the dispersion term, the (anisotropic) electrostatic potential was included. At room temperature, their rate constant was found to be an order of magnitude too large with respect to the CRESU measurement. At ultra low temperatures ($T \lesssim 1$ K), the dipole−dipole potential was found to dominate, as expected, and an analytical rate constant of the form $k_{T\to 0}(T) = 4.42 \times 10^{-10}(T)^{1/6}$ was predicted by using perturbation theory.[25] We note that this result is roughly consistent with our values. We did not attempt, however, to match our model with the perturbation theory since this latter has not been generalized to asymmetric species which are investigated in the following.

Further comparisons between our semiempirical model and low temperature measurements are illustrated in Figures 2−5. In addition to $CN(X^2\Sigma^+)$, the following radicals were investigated to provide a variety of reactions: atomic carbon, $C(^3P)$, the methylidyne radical, $CH(X^2\Pi)$, and the ethynyl radical $C_2H(X^2\Sigma^+)$. In the case of CN (Figure 2), the following CRESU reactions were analyzed: CN + O_2;[24] CN + C_2H_6, CN + C_2H_2, and CN+C_2H_4;[26] CN + $CH_2C_2H_2$ (allene) and CN + CH_3C_2 H (methyl acetylene).[27] Again, the agreement between our model and the CRESU data is generally good (within 40%), except for the CN + C_2H_6 reaction. The latter, however, is the only CN reaction among those studied for which the activation energy is positive at room temperature. Indeed, the rate constant has a minimum value at about 300 K but increases at both higher and lower temperature.[26] As a result, CN + C_2H_6 does not belong to the standard class of fast reactions, as defined in the previous section. On the other hand, the transition state theory of Georgievskii and Klippenstein[11] has been successfully applied to CN + C_2H_6 which appears as the prototype of reactions involving two transition states. We also observe in Figure 2 that the temperature dependences of the rates are rather moderate, except for CN + C_2H_6 and CN + O_2 where the values at the lowest measured temperatures differ from the room temperature values by more than a factor of 2. Note that for the radical−radical reaction CN + O_2, the capture rate constants at 10 and 30 K were divided by a factor of 3 to allow for electronic degeneracy (assuming that the reaction occurs only over the lowest $^2A''$ surface, see Sims et al.[24]). The α, β, and γ fitting coefficients of the above CN reactions are given in Table 1.

In the case of atomic carbon, the following CRESU reactions were analyzed: C + NO and C + O_2;[28] C + C_2H_2, C + C_2H_4, C + $CH_2C_2H_2$, and C + CH_3C_2H;[29] C + C_3H_6 (propene).[30] The agreement between our model and the experimental data is less good than for CN but is still within a factor of 2, as shown in Figure 3. It should be noted that the capture temperatures T_1 = 5 K and T_2 = 15 K were found here to provide the best results (and to force the rate maxima to lie at ∼10 K). This reflects

TABLE 1: Fitting Coefficients α ($cm^3\ s^{-1}$), β, and γ (K), Eq 4, to the Rate Constants of Various CN Reactions Measured with the CRESU Apparatus[a]

reaction	α	β	γ
$CN + NH_3$	2.91 (−11)	−1.59	29.0
$CN + O_2$	2.38 (−11)	−0.937	18.2
$CN + C_2H_2$	2.58 (−10)	−0.367	8.80
$CN + C_2H_4$	2.56 (−10)	−0.399	9.31
$CN + C_2H_6$	2.99 (−11)	−1.63	29.7
$CN + CH_2C_2H_2$	3.96 (−10)	−0.128	4.86
$CN + CH_3C_2H$	4.06 (−10)	−0.161	5.40

[a] Fits are only valid in the temperature range 10−295 K. Powers of ten are given in parentheses.

TABLE 2: Fitting Coefficients α ($cm^3\ s^{-1}$), β, and γ (K), Eq 4, to the Rate Constants of Various Atomic Carbon Reactions Measured with the CRESU Apparatus[a]

reaction	α	β	γ
$C + NO$	1.21 (−10)	−0.457	5.14
$C + O_2$	4.13 (−11)	−0.453	5.11
$C + C_2H_2$	3.11 (−10)	−0.187	2.91
$C + C_2H_4$	2.68 (−10)	−0.271	3.61
$C + C_3H_6$	2.71 (−10)	−0.292	3.78
$C + CH_2C_2H_2$	3.24 (−10)	−0.190	2.94
$C + CH_3C_2H$	2.51(−10)	−0.328	4.08

[a] Fits are only valid in the temperature range 5−295 K. Powers of ten are given in parentheses.

TABLE 3: Fitting Coefficients α ($cm^3\ s^{-1}$), β, and γ (K), Eq 4, to the Rate Constants of Various CH Reactions Measured with the CRESU Apparatus[a]

reaction	α	β	γ
$CH + D_2$	8.41 (−11)	−0.783	7.83
$CH + NO$	1.33 (−10)	−0.443	5.02
$CH + O_2$	3.66 (−11)	−0.526	5.71
$CH + NH_3$	1.38 (−10)	−0.514	5.61
$CH + CH_4$	9.01 (−11)	−0.729	7.38
$CH + C_2H_2$	4.02 (−10)	−0.106	2.25
$CH + C_2H_4$	2.94 (−10)	−0.257	3.49
$CH + C_2H_6$	2.28 (−10)	−0.370	4.42

[a] Fits are only valid in the temperature range 5−295 K. Powers of ten are given in parentheses.

TABLE 4: Fitting Coefficients α ($cm^3\ s^{-1}$), β, and γ (K), Eq 4, to the Rate Constants of Various C_2H Reactions Measured with the CRESU Apparatus[a]

reaction	α	β	γ
$C_2H + O_2$	4.06 (−11)	−0.455	5.12
$C_2H + C_2H_2$	1.07 (−10)	−0.624	6.52
$C_2H + C_2H_4$	1.00 (−10)	−0.672	6.91
$C_2H + C_3H_6$	1.86 (−10)	−0.432	4.93
$C_2H + CH_2C_2H_2$	1.82 (−10)	−0.414	4.79
$C_2H + CH_3C_2H$	1.72 (−10)	−0.471	5.25

[a] Fits are only valid in the temperature range 5−295 K. Powers of ten are given in parentheses.

the fact that low temperature rate constants are in general lower for $C(^3P)$ than for $CN(X^2\Sigma^+)$. This is further discussed below in the case of CH and C_2H. We note that for $C + O_2$, the capture rate constants at 5 and 15 K were divided by a factor of 3 to allow for electronic degeneracy (assuming that reaction occurs only on the singlet and triplet surfaces leading to the exothermic products $CO(X^1\Sigma^+\ 0) + O$, see Chastaing et al.[30]). On the other hand, no degeneracy factor was employed for C+NO for which all 36 surfaces lead adiabatically to exothermic products.[31] Note that temperature dependent degeneracy factors including spin−orbit effects are negligible at very low temperature and were therefore ignored here. These effects have been, however, found to be crucial at higher temperature for both $C + NO$ and $C + O_2$.[31,32] The α, β, and γ fitting coefficients of the above atomic carbon reactions are given in Table 2.

In the case of CH, the following CRESU reactions were analyzed: $CH + D_2$;[33] $CH + NO$, $CH + O_2$, and $CH + NH_3$;[34] $CH + CH_4$, $CH + C_2H_2$, $CH + C_2H_4$, $CH + C_2H_6$.[35] Reactions that proceed by pressure-dependent association or association in the high-pressure limit (e.g., $CH+H_2$) were not considered. The polarizability of CH was taken from the theoretical calculations of Manohar and Pal.[36] The agreement between our model and the experimental data is still within a factor of 2, as shown in Figure 4, except for $CH + D_2$ below 50 K where our model exceeds the CRESU data by up to a factor of 3. As for atomic carbon, the capture temperatures $T_1 = 5$ K and $T_2 = 15$ K were found to provide the best results. It is not clear why the present model fails so spectacularly for D_2 below 50 K (the activation energy is close to zero at 300 K, see Brownsword et al.[33]), but this could be related to the small moment of inertia, i.e., high rotational angular velocity, of D_2.[12] We also note that for all CH reactions except $CH + O_2$ our model exceeds the CRESU data at the lowest measured temperatures (see in particular the sharp decrease of the rate for $CH + C_2H_6$ below 50 K). Thus, the experimental rates are found to "saturate", in all 8 cases except O_2, at ~50 K, in contrast to C and CN. One of the possible explanations could be the anisotropy of the real potential, entirely neglected in our model. The α, β, and γ fitting coefficients of the above CH reactions are given in Table 3.

In the case of C_2H, the following CRESU reactions were analyzed: $C_2H + O_2$, $C_2H + C_2H_2$, $C_2H + C_2H_4$, and $C_2H + C_3H_6$;[37] $C_2H + CH_2C_2H_2$ and $C_2H + CH_3C_2H$.[27] The polarizability of C_2H was taken from the theoretical calculations of Herbst and Woon.[38] The agreement between our model and the experimental data is here within a factor of 2 for all systems above 25 K, as shown in Figure 5. At temperatures below 25 K, our model overestimates the rate constants of $C_2H + C_2H_2$, $C_2H + C_2H_4$, and $C_2H + C_3H_6$, with discrepancies up to a factor of 4 with respect to CRESU data. As for CH, it is not clear why our model fails for these reactions below 50 K. We note that in the case of $C_2H + C_3H_6$ the sharp decrease of the rate constant below 50 K was possibly attributed by Vakhtin et al.[39] to the effect of clustering of the reactant molecules. In their paper, Chastaing et al.[37] noted that the rate constants for C_2H are in general a factor of 2−3 smaller than those for the corresponding reactions of the (isoelectronic) CN radical. They attributed this difference to either the increase in structural complexity or the lower dipole moment of C_2H (0.8 D vs 1.45 D for CN). This latter point is also consistent with the fact that the rate constants for $CH + C_2H_2$ and $CH + C_2H_4$ at very low temperatures are very similar to those for the corresponding reactions of CN, see Figures 2 and 4 (the CH dipole moment is 1.46 D). This suggests that the inclusion of the anisotropic electrostatic potential might improve the agreement between our model and CRESU data. We stress again, however, that the anisotropic capture theory has yet to be extended to asymmetric species. The α, β, and γ fitting coefficients of the above C_2H reactions are given in Table 4.

It is important to emphasize, finally, that in contrast to ion−molecule reactions for which mass spectrometric techniques allow the observation of both product and reagent ions, no information is obtained about the products of a neutral−neutral reaction with the CRESU method.[16] Of course, neither can the present model predict the reaction products. We therefore refer

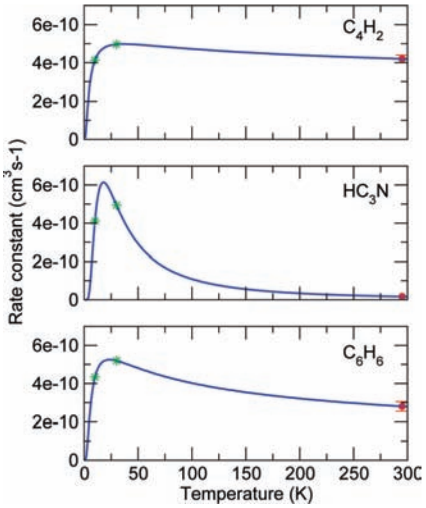

Figure 6. Same as Figure 1 for the CN radical reacting with C_4H_2, HC_3N, and C_6H_6. See text for details and references.

the reader to the experimental publications for the likely products of the above radical reactions (see also below). Furthermore, it should be noted that a number of experimental studies of products have been performed at room temperature or above by different groups working on neutral systems. The Leone group, in particular, has recently reported the direct detection of isomer-specific products for CN and C_2H radical reactions at room temperature.[40,41] These experiments used synchrotron radiation coupled with time-resolved multiplexed mass spectrometry. Crossed beam experiments have been also conducted, possibly combined with ab initio calculations, to assign the products of radical reactions (see, e.g., Geppert et al.[31] and Zhang et al.[42]).

Predictions for CN Radical Reactions with C_4H_2, HC_3N, and C_6H_6. As mentioned in the introduction, reactions of CN with hydrocarbons and nitriles are of particular importance in the context of Titan's chemistry. Although the reaction products cannot be inferred experimentally at very low temperatures (as explained above), these reactions are generally divided in three classes:[43] (a) abstraction of an hydrogen atom from saturated hydrocarbons, e.g., $CN + C_2H_6 \rightarrow HCN + C_2H_5$; (b) addition to unsaturated C−C bonds followed by H atom elimination, e.g., $CN + C_2H_2 \rightarrow H + C_2HCN$; (c) addition to CN bond followed by H elimination, e.g., $CN + HCN \rightarrow H + C_2N_2$. Reactions belonging to class b are expected to be the fastest. We have selected three reactions belonging to classes b and c whose rates are larger than 10^{-11} cm^3 s^{-1} at 295 K: $CN + C_4H_2$ (k(295 K) = 4.2×10^{-10} cm^3 s^{-1}),[43] $CN + HC_3N$ (k(295 K) = 1.7×10^{-11} cm^3 s^{-1})[44] and $CN + C_6H_6$ (k(295 K) = 2.8×10^{-10} cm^3 s^{-1}).[45] On Titan, the reaction of CN with C_4H_2 is expected to form HC_5N, while the reaction with HC_3N is likely a source of C_4N_2. The products of the $CN + C_6H_6$ reaction have been observed to be $C_6H_5CN + H$,[46] and it is the only reaction known to produce cyanobenzene. By assumption of zero activation energies, these three reactions should become faster at low temperature. The results of our semiempirical approach are presented in Figure 6, using the capture temperatures T_1 = 10 K and T_2 = 30 K, as suggested by the available CRESU data for CN reactions (see above). The polarizability of HC_3N was taken from the ab initio calculations of Fowler and Diercksen.[47] The polarizability and ionization potential of C_4H_2 were taken Karamanis and Maroulis[48] and Ramos et al.,[49] respectively. It can be seen in Figure 6 that the rate temperature dependences are negative but rather weak for reactions of CN with C_4H_2 and C_6H_6. This implies that using our low temperature rate constants instead of the rates measured at room temperature in Titan's photochemical models will not significantly change the calculated densities of HC_5N and C_6H_5CN. The reaction of $CN + HC_3N$ shows a stronger temperature dependence. However, only Lavvas et al. include the latter reaction in their model.[50,51] An activation energy of ∼1.5 kcal mol^{-1} was actually postulated by Halpern et al.[44] suggesting a rate constant of ∼ 1×10^{-13} cm^3 s^{-1} at 100 K. In contrast, our model predicts a rate constant of ∼1×10^{-10} cm^3 s^{-1} at 100 K, that is 3 orders of magnitude greater. It is clear that measurements at low temperature would discriminate between both predictions. Nevertheless this reaction does not have much impact on Titan's atmosphere as it is only a minor channel for the production of C_4N_2.[50,52] The α, β, and γ fitting coefficients of the three above CN reactions are given in Table 5.

TABLE 5: Fitting Coefficients α (cm^3 s^{-1}), β, and γ (K), Eq 4, to the Rate Constants of Three CN Reactions Relevant for Titan[a]

reaction	α	β	γ
$CN + C_4H_2$	4.26 (−10)	−0.139	5.04
$CN + HC_3N$	1.85 (−11)	−1.93	34.5
$CN + C_6H_6$	2.87 (−10)	−0.391	9.19

[a] Fits are only valid in the temperature range 10−295 K. Powers of ten are given in parentheses.

Conclusions

A simple, semiempirical, model has been presented to extend the rate constants of fast neutral−neutral reactions from room temperature down to 5−10 K. Predicting rate constants down to these very low temperatures is crucial for Titan's and interstellar chemistry. The present model has been shown to apply to radical-molecule reaction for which the activation energy is zero or negative at room temperature and the rate is greater than 10^{-11} cm^3 s^{-1}: good agreement with CRESU experimental data (to within a factor of 2 above 25 K) was observed for a sample of 26 radical reactions involving atomic carbon, CN, CH, and C_2H. The two major exceptions are $CN + C_2H_6$, for which the activation energy is positive at room temperature, and $CH + D_2$. At temperatures lower than 25 K, discrepancies up to a factor of 4 have been observed for a few systems, possibly reflecting the contribution of the anisotropic electrostatic potential. Our approach is based on the long-range capture theory, combined with room temperature data. Only the long-range isotropic dispersion potential is considered in the capture calculations and, as a result, the present model simply requires the ionization potentials and the polarizabilities of the reactants. It is therefore easily generalized to any fast reaction involving large polyatomic (asymmetric) molecules provided the reaction obeys the above criteria. As an example, for the $CN + HC_3N$ reaction, our model was found to predict a large rate below 200 K, in disagreement with the postulated (positive) activation energy.[44] Obviously, our approach has to be further checked against the full amount of available low temperature data. This will be done in future works. We believe, still, that the present model should provide an accuracy better than a factor of 2 in many favorable cases. Such a precision is clearly valuable at the current level of astrochemical modeling. Finally, it should be noted that for a number of important neutral reactions no kinetic data exist. For these our model is inapplicable and semiempirical arguments[17] and/or high level ab initio calculations are required.

Appendix

We give below the expressions for the fitting coefficients α, β, and γ (eq 4) as functions of k_1, k_2, and k_3. Temperatures will be denoted T_1, T_2, and T_3 so that formulas can be adapted to any particular choice of temperatures

$$\alpha = \frac{k_1(T_3)^{\beta}}{T_1^{\beta}\exp(-\gamma/T_1)} \tag{5}$$

$$\beta = \frac{\ln(k_1/k_2) - \gamma[(1/T_2) - (1/T_1)]}{\ln(T_1/T_2)} \tag{6}$$

$$\gamma = \frac{[\ln(k_1/k_2)\ln(T_2/T_3)/\ln(T_1/T_2)] - \ln(k_2/k_3)}{([(1/T_2) - (1/T_1)]\ln(T_2/T_3)/\ln(T_1/T_2)) + [(1/T_2) - (1/T_3)]} \tag{7}$$

It should be noted that because k_1 and k_2 are here both obtained from the capture formula, eq 1, the ratio (k_1/k_2) depends only on the temperature ratio (T_1/T_2). As a result, β and γ are linearly dependent

$$\beta = \frac{\ln[(T_1/T_2)^{1/6}] - \gamma[(1/T_2) - (1/T_1)]}{\ln(T_1/T_2)} \tag{8}$$

Hence, our model actually requires only two independent parameters.

Acknowledgment. A.F. and L.W. acknowledge support by the French National Research Agency (ANR-08-BLAN-0225-01) and the French National Program "Physico-Chimie du Milieu Interstellaire".

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JP905609X