

## Kinetics of the Reaction of Amino Radicals with Olefins

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Absolute rate constants for the reaction of  $\text{NH}_2$  radicals with olefins have been determined over the temperature range 300–500 K using a flash photolysis-laser resonance absorption technique. The Arrhenius parameters are similar for all the compounds studied, ethylene, propylene, and the four butenes:  $A = 1\text{--}3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ;  $E = 4\text{--}4.3 \text{ kcal mol}^{-1}$ . The measured rate constants correspond to the addition of  $\text{NH}_2$  to the double bond. The slight dependence of the addition rate constant upon alkyl substitution of the double bond suggests a very low electrophilic character for  $\text{NH}_2$  in this reaction. A slight pressure dependence of the rate constant for ethylene has been detected. The reactivity of  $\text{NH}_2$  is compared to that of the isoelectronic OH and  $\text{CH}_3$  radicals.

## Introduction

The amino radical is certainly the most important intermediate species in all photochemical and radiochemical processes of ammonia. In contrast to the very large number of studies of ammonia chemistry, practically no attention has been given to the reactivity of  $\text{NH}_2$  radicals. This is particularly true for the reaction of this radical with hydrocarbons.

The lack of kinetic data on the  $\text{NH}_2$  reactions is particularly surprising when compared to the volume of information available on the reactivity of the isoelectronic OH and  $\text{CH}_3$  radicals. Certainly it would be of interest to compare the kinetics parameters concerning these three radicals in certain fundamental reactions such as their addition to double bonds or hydrogen abstraction from alkanes.

In this work, absolute rate constants for  $\text{NH}_2$  reactions with a series of olefins have been determined over the temperature range 300–500 K by flash photolysis, using laser resonance absorption detection. The advantage of this technique for  $\text{NH}_2$  detection is essentially its high sensitivity independent of the pressure.

Information on the reactions of amino radicals with unsaturated compounds are indeed scarce in the literature. It was shown that  $\text{NH}_2$  adds to the double bond of ethylene in the photolysis of the  $\text{NH}_3\text{--C}_2\text{H}_4$  system<sup>1</sup> and a rate constant of about  $10^7 \text{ M}^{-1} \text{ s}^{-1}$  for the reaction of  $\text{NH}_2$  with propylene was deduced from radiolysis investigations of ammonia.<sup>2,3</sup> On the other hand, the inefficiency of  $\text{NH}_2$  addition to olefins was emphasized<sup>4,5</sup> and calculations of the potential energy surfaces of the reaction with ethylene yielded very high activation energies.<sup>5</sup> In a preliminary study from this laboratory<sup>6</sup> the Arrhenius parameters were reported for the reaction of  $\text{NH}_2$  with propylene. This study is extended here to ethylene and the butenes and the results are discussed in more detail.

## Experimental Section

The experimental apparatus and procedure have been described in preceding papers.<sup>6,7</sup>  $\text{NH}_2$  radicals are produced mostly in their ground vibrational state by flash photolysis of ammonia through ordinary quartz. The concentration is monitored by resonance absorption using a single mode continuous wave dye laser (Spectra Physics 580) tuned on the strong  $\text{NH}_2$  absorption line at 597.73 nm. The laser spectral width is about 50 MHz and therefore much narrower than the Doppler width of the absorption line (1–3 GHz). Under these conditions the Beer–Lambert law is obeyed and absorptions are always measured at the maximum of the line, resulting in high radical detection

sensitivity. The kinetics of  $\text{NH}_2$  decay are generally measured with an initial absorption of 10% and an optical path length of 28 m. This corresponds to an initial  $\text{NH}_2$  concentration of  $10^{11} \text{ molecules cm}^{-3}$  at low pressure and about  $3\text{--}5 \times 10^{11} \text{ molecules cm}^{-3}$  at atmospheric pressure. In a few experiments, a signal averager has been used, increasing the radical detection sensitivity by one order of magnitude and therefore allowing measurements of decay kinetics with  $\text{NH}_2$  initial concentrations around  $10^{10} \text{ molecules cm}^{-3}$ .

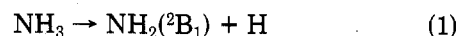
Experiments were carried out with olefin pressures ranging from 10 to 100 torr. For such pressures and small radical concentrations, any radical recombination could not be detected in competition with the reaction  $\text{NH}_2 + \text{olefin}$ .

Activation energies were measured by enclosing both the flash lamps and reaction cell in a furnace which could be heated to 240 °C.

Gas mixtures were prepared using a conventional vacuum line fitted with teflon–glass valves. Ammonia (99.995%) was dried over sodium and distilled at low temperature. Olefins from l'Air Liquide were degassed by distillation at low temperature, and used without further purifications. According to the manufacturer, the purity levels were as follows: ethylene and isobutane, 99.95%; propylene, 1- and 2-butenes, isobutane, 99.0%. The impurities were essentially composed of alkanes, which are less reactive than olefins, and other olefins.

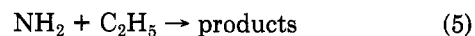
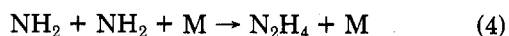
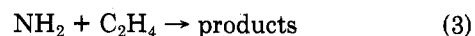
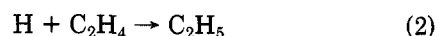
## Results and Discussion

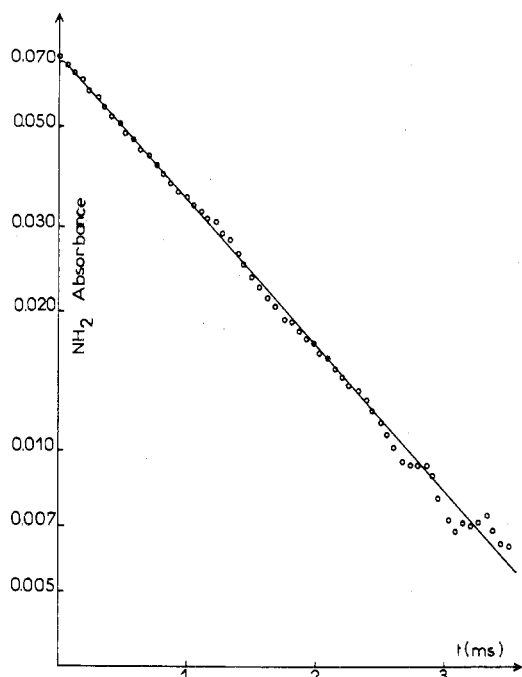
By flashing ammonia with light of  $\lambda > 180 \text{ nm}$ , only dissociation reaction 1 is observed.  $\text{NH}_2$  is obtained in its



ground electronic and vibrational state,<sup>9</sup> most of the excess energy being absorbed by the hydrogen atom.<sup>10</sup> However, the possibility of the formation of excited  $\text{NH}_2$  was suggested,<sup>10</sup> but this could not affect the present measurements, as only the ground state was monitored and a rapid relaxation must occur at the high pressure used.

In the presence of an olefin the following reaction scheme can be envisaged, in the particular case of ethylene:





**Figure 1.** Semilog plot of the  $\text{NH}_2$  absorbance decay in the presence of 35 torr of ethylene at 346 K. The ammonia pressure was 3 torr. Under these conditions, the  $\text{NH}_2$  extinction coefficient at the maximum of the absorption line is  $6000 \pm 1000 \text{ M}^{-1} \text{ cm}^{-1}$ , resulting in an initial  $\text{NH}_2$  concentration of  $4.2 \times 10^{-9} \text{ M}$ .

For an olefin pressure greater than 10 torr, which is always the case in our experiments, reaction 2 is complete during the flash time. Thus, the rate  $\text{NH}_2$  decay can be expressed as

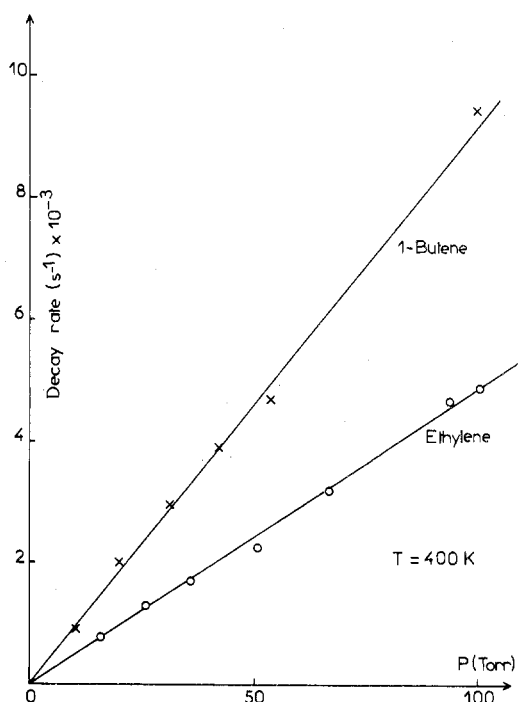
$$-d[\text{NH}_2]/dt = k_3[\text{NH}_2][\text{C}_2\text{H}_4] + 2k_4[\text{NH}_2]^2 + k_5[\text{NH}_2][\text{C}_2\text{H}_5] \quad (\text{I})$$

the initial concentration of  $\text{NH}_2$  and  $\text{C}_2\text{H}_5$  being equal.

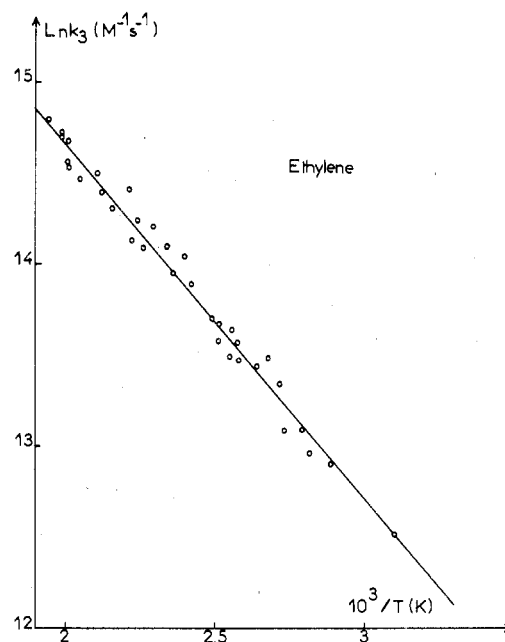
The recombination rate constants  $k_4$  and  $k_5$  have been measured in our laboratory. The value of  $k_4$  is pressure dependent up to several hundred torr, the value of the high pressure limit being<sup>11</sup>  $k_4(\infty) = 1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_5$  was measured in the presence of a low olefin pressure (0.1–0.3 torr) so that reaction 2 was still efficient and  $\text{NH}_2$  radicals disappeared essentially by reaction 5:  $k_5 = 1.5\text{--}2.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for ethyl, isopropyl, and *tert*-butyl radicals at room temperature.<sup>8</sup>

Since the value of  $k_3$  was about five orders of magnitude smaller than the radical recombination rate constants, much care was taken to set the conditions of measurements so that reactions 4 and 5 could be neglected, reaction 3 then being considered as the only path for the disappearance of  $\text{NH}_2$ . This was achieved by always using the lowest possible initial concentration of  $\text{NH}_2$  (10% initial absorption), and by using olefin pressures higher than 10–20 torr, up to 100 torr. Higher pressures could not be used, especially for the butenes, because of possible olefin photolysis.

Under these conditions the  $\text{NH}_2$  decay showed pseudo-first-order kinetics as seen in Figure 1. However, for the low absorption used, the signal-to-noise ratio was not sufficient for us to be completely certain that the decay was strictly first order. We were able to verify that no radical recombination occurred to a significant extent by showing that the  $\text{NH}_2$  decay rate was independent of the  $\text{NH}_2$  initial concentration. No deviation larger than experimental errors could be observed except in a few experiments at the lowest pressures and temperatures for which the rate of reaction 3 was too small.



**Figure 2.** Plots of the  $\text{NH}_2$  decay rate  $K$  against olefin concentration for ethylene and 1-butene at 400 K. The ammonia pressure was 3 torr and no diluent gas was added. The decay rate only due to reactions 4 and 5 at very low pressures of olefin would be about  $50\text{--}100 \text{ s}^{-1}$  for 10% initial absorption.



**Figure 3.** Arrhenius plot of  $\ln k_3$  against  $1000/T$  for ethylene.

Moreover, if the disappearance of  $\text{NH}_2$  is only due to reaction 3 the decay rate must be proportional to the olefin pressure. This is generally true for all the compound studied. Figure 2 illustrates the cases for ethylene and 1-butene at a temperature of 400 K and for pressures varying from 10 to 100 torr. Each point is generally determined from the average of three different decays.

The temperature dependence of  $k_3$  has been studied between 300 and 500 K. For each compound  $k_3$  was measured for about six different pressures and eight different temperatures. The Arrhenius plots obtained in the cases of ethylene and isobutene are given in Figures 3 and 4. Similar plots are obtained with all the compounds studied, showing that reaction 3 occurs with a

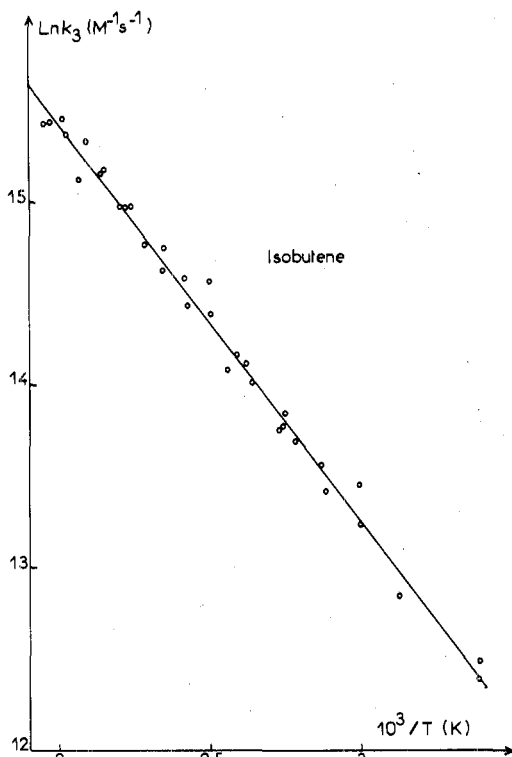


Figure 4. Arrhenius plot of  $\ln k_3$  against  $1000/T$  for isobutene.

TABLE I: Arrhenius Parameters and Room Temperature Rate Constants for the Reaction of  $\text{NH}_2$  with Olefins and Isobutane

	$10^{-5}A$ , $\text{M}^{-1} \text{s}^{-1}$	$E$ , kcal $\text{mol}^{-1}$	$10^{-5}k_3$ , $\text{M}^{-1} \text{s}^{-1}$ (300 K)
ethylene	1.2	$3.95 \pm 0.2$	$1.65 \pm 0.25$
propylene	2.8	$4.30 \pm 0.2$	$2.15 \pm 0.35$
isobutene	4.6	$4.50 \pm 0.2$	$2.55 \pm 0.40$
1-butene	2.8	$4.10 \pm 0.2$	$3.00 \pm 0.45$
<i>trans</i> -2-butene	3.5	$4.25 \pm 0.2$	$2.95 \pm 0.45$
<i>cis</i> -2-butene	3.3	$4.30 \pm 0.2$	$2.55 \pm 0.40$
isobutane	2.4	$5.00 \pm 0.2$	$0.62 \pm 0.09$

significant activation energy. The Arrhenius plots are reasonable straight lines, indicating that there is no change in the activation energy over the range of temperature examined.

Preexponential factors, activation energies deduced from least-squares treatment of the data, and rate constants at room temperature are given in Table I. The experimental error in the rate constants determined at each temperature is about 15% while the errors in the activation energies were evaluated to be 0.2 kcal/mol for all the olefins. For comparison, the Arrhenius factors obtained with isobutane are also included in Table I.

The first characteristic of these results is that the reactivity of  $\text{NH}_2$  with olefins is rather weak and very similar for all the compounds of the series. Activation energies are around 4 kcal  $\text{mol}^{-1}$  and the rate constants at room temperature are all between  $1.5$  and  $3 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$ .

No agreement can be found between these results and preceding rate constant determinations<sup>3,4</sup> or activation energy calculations.<sup>5</sup> The best correlation can be made with the work by Schurath et al.<sup>1</sup> According to their experimental conditions and the relative yield of the end products, a rate constant of  $1\text{--}5 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$  can be evaluated for the addition of  $\text{NH}_2$  to ethylene, in agreement with the present finding.

It is important to recognize that our results obtained from flash photolysis experiments are deduced only from the disappearance of  $\text{NH}_2$  and do not in themselves

provide information on the types of products formed. The question arises as to whether the rate constants measured correspond to the addition reaction of  $\text{NH}_2$  to the double bond or, at least partly, to an hydrogen abstraction from the olefin.

The case for ethylene must be considered apart from that of the other compounds since the vinyl C-H bond energy (103 kcal  $\text{mol}^{-1}$ ) is much higher than that of the allyl C-H bond (88 kcal  $\text{mol}^{-1}$ ). The competition of an hydrogen abstraction with an addition reaction should therefore be very different for ethylene and for the other olefins.

Experimentally it has been found that the addition of  $\text{NH}_2$  to ethylene is an important process in the steady photolysis of an ammonia-ethylene mixture<sup>1</sup> as seen by end product analysis. Energy considerations are not in favor of hydrogen abstraction. Indeed the activation energy for the abstraction of the tertiary hydrogen atom in isobutane ( $D_0(\text{C-H}) = 92 \text{ kcal mol}^{-1}$ ) is significantly higher than the activation energy measured for the reaction of  $\text{NH}_2$  with ethylene ( $D_0(\text{C-H}) = 103 \text{ kcal mol}^{-1}$ ). Moreover recent investigations<sup>8</sup> have shown that the activation energy for hydrogen abstraction from methane by  $\text{NH}_2$  is higher than twice the value reported in this study for ethylene although the C-H bond energy in methane (104 kcal  $\text{mol}^{-1}$ ) is about the same as that in ethylene. It is thus expected that the activation energy for hydrogen abstraction from ethylene is much higher than 4 kcal  $\text{mol}^{-1}$  and if such a process did occur in the range of temperature studied, a significant curvature of the Arrhenius plot should be observed. It is therefore likely that the rate constant measured for ethylene corresponds only to the addition process, the abstraction reaction being a higher energy pathway.

In order to substantiate this conclusion, we studied the steady photolysis of ammonia at 206.2 nm, using a microwave powered iodine lamp, in the presence successively of isobutane and ethylene. The experimental conditions were such that all  $\text{NH}_2$  radicals were scavenged by these compounds and could not react by radical recombination. The disappearance of  $\text{NH}_3$  was measured by UV absorption spectrometry at 213 nm. In the presence of 250 torr of isobutane no ammonia disappeared since the only possible reaction of  $\text{NH}_2$  was by hydrogen abstraction, which re-forms ammonia. This reaction was taken as an actinometer by measuring the amount of molecular hydrogen formed in the reaction of hydrogen atoms with isobutane:  $\Phi_{\text{H}_2} = 0.85 \pm 0.1$ .<sup>12</sup> In the presence of 200 torr of ethylene ammonia disappeared with a quantum yield of  $0.80 \pm 0.2$ . Although the accuracy of the measurements was not better than 25% since the photolysis of ammonia had to be limited to less than 5% to prevent secondary reactions with the photolytic products, the result shows clearly that the principal reaction of  $\text{NH}_2$  with ethylene is the addition process.

The low energy of the allyl C-H bond in propylene and butenes could make hydrogen abstraction competitive with the addition process. However the addition reaction is still predominant. Indeed ammonia, photolyzed in the presence of propylene under the same conditions as in the presence of ethylene, also disappeared with a quantum yield of  $0.80 \pm 0.2$ . This shows that the hydrogen abstraction process if it occurs is not more important than in the case of ethylene. Similar experiments were not possible with the butenes due to the presence of their UV absorption tail, overlapping the ammonia spectrum. However, the similarity of the activation energies for all the olefins studied suggests a unique reaction process for these compounds. It would be surprising that both ad-

TABLE II: Comparison of Arrhenius Parameters and Room Temperature Rate Constants for the Reaction of OH, NH<sub>2</sub>, and CH<sub>3</sub> with Propylene

	log <i>k</i> , M <sup>-1</sup> s <sup>-1</sup> (300 K)	log <i>A</i> , M <sup>-1</sup> s <sup>-1</sup>	<i>E</i> , kcal mol <sup>-1</sup>	ref
OH	10.1	9.40	(-1.08)	14
NH <sub>2</sub>	5.35	8.45	4.30	this work
CH <sub>3</sub>	2.85	8.22	7.4	16

dition and hydrogen abstraction processes have the same Arrhenius parameters in all cases. Also, if an hydrogen abstraction occurred to a significant extent on the allylic hydrogen atoms of 1-butene (two allylic H) and 2-butene (six allylic H), the preexponential factor should be significantly different as observed in the case of propane and butane for the abstraction of secondary hydrogen atoms.<sup>8</sup>

It can be concluded that addition is the main reaction in the case of ethylene and propylene. Obviously the addition process still occurs in the case of butenes since the Arrhenius parameters are about the same for all compounds. However the present results do not allow us to reject the possibility of an hydrogen abstraction from the butenes. For OH and CH<sub>3</sub> radicals, both addition and hydrogen abstraction have been shown to occur.<sup>13,14</sup>

Only accurate measurements of the yield of end products in steady photolysis experiments would supply the necessary information for the determination of the relative importance of the two processes. However, due to the difficulty of measuring minute amounts of amino compounds (octylamines in the case of butenes) the determination of reliable quantum yield does not seem possible.

The observed variations in rate constants and Arrhenius parameters from one olefin to another are not much larger than the standard deviations in the experiments themselves. Thus the reactivity of the NH<sub>2</sub> radical is not significantly sensitive to alkyl substitution of the double bond. This is consistent with the very small electrophilic character of NH<sub>2</sub> in the olefinic bond attack. A marked electrophilic character would have resulted in a significant increase of the addition rate constant from ethylene to the butenes.

If one compares this behavior of NH<sub>2</sub> to that of the isoelectronic OH and CH<sub>3</sub> radicals, it appears more similar to that of CH<sub>3</sub> and other alkyl radicals than to that of the OH radical.<sup>15</sup> One has to be careful, however, in asserting the electrophilic character of OH radicals in its reactions with alkyl substituted olefins, to be sure that the slight increase in rate constant with the increasing alkyl substitution<sup>16</sup> is not due to hydrogen abstraction.<sup>13</sup>

The activation energies and the rate constants at room temperature for the reaction of NH<sub>2</sub> with olefins are intermediate between those of CH<sub>3</sub> and OH radicals. This is shown in Table II where the Arrhenius parameters and rate constants are compared in the case of propylene. The differences essentially arise from the activation energies which are around 7–8 kcal mol<sup>-1</sup> for CH<sub>3</sub> and 4 kcal mol<sup>-1</sup> for NH<sub>2</sub> while a slightly negative temperature coefficient is obtained for OH,<sup>14</sup> for all the olefins of the series.

Having deduced that the reaction of NH<sub>2</sub> with ethylene is an addition process, the product of the first step is a β-aminoethyl radical which needs to be stabilized by collisions with a third body. One must therefore expect a pressure dependence of the rate constant of this reaction, as has been observed for the addition of OH to ethylene.<sup>17,18</sup>

Our results suggest that this pressure dependence will be very small at pressure higher than 10–15 torr. Indeed, the good linearity of the plot in Figure 2 shows that there is no variation of the rate constant between 10 and 100 torr. The small rate constant did not permit accurate measurements at lower ethylene pressures. However, a few experiments could be performed at 500 K using 0.5 torr of ammonia and 1 torr of ethylene. The signals from 100 flashes were accumulated in a signal averager allowing measurements at very low radical concentrations.

The rate constant obtained under these conditions is approximately half the value obtained at high pressure. These experiments show that a slight pressure effect occurs at a few torr of total pressure, but a detailed investigation of such small effect with acceptable accuracy was not practicable.

The pressure effect observed in the case of the addition reaction of OH to ethylene is much more important than in the case of NH<sub>2</sub>.<sup>17,18</sup> The extra bond to hydrogen in NH<sub>2</sub> compared to OH, which provides an extra vibrational mode for energy distribution, certainly results in a minor effect. The reaction of OH with ethylene is more exothermic (35 kcal mol<sup>-1</sup>) than that of NH<sub>2</sub> (17 kcal mol<sup>-1</sup>) and consequently the radical produced must undergo a larger number of collisions in order to be stabilized. However, the exothermicity may not be large enough to explain the observed difference.

An alternative explanation<sup>19</sup> can be found in the preexponential factors which, from Table II, are 10 times larger for OH than for NH<sub>2</sub>. Since the entropy changes of the addition reactions should be similar for the two radicals, it follows that the frequency factors for the decomposition of the adduct radicals (the reverse of the addition reactions) will reflect about the same factor of 10. This implies that the newly formed OH adduct radical will decompose very roughly 10 times faster than the newly formed NH<sub>2</sub> adduct, and therefore is more difficult to stabilize by collision.

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