Kinetics of Hydrogen Abstraction by NH_2 Radicals from Alkanes in the Gas Phase. A Flash Photolysis–Laser Resonance Absorption Study

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Abstract: Absolute rate constants for hydrogen abstraction reactions by NH_2 radicals in a series of alkanes and molecular hydrogen have been determined between 300 and 520 K. Measurements were performed by flash photolysis using laser resonance absorption detection of NH_2. This technique allowed the determination of low rate constants, owing to its high sensitivity independent of pressure. The Arrhenius expressions obtained were the following, with A in $M^{-1}\ s^{-1}$ and E in kcal mol^{-1}: isobutane, $2.3 \times 10^8 \exp[-(4.90 \pm 0.22/RT)]$; *n*-butane, $7.0 \times 10^8 \exp[-(6.10 \pm 0.25/RT)]$; propane, $4.5 \times 10^8 \exp[-(6.15 \pm 0.25/RT)]$; ethane, $3.7 \times 10^8 \exp[-(7.15 \pm 0.28/RT)]$; hydrogen, $1.26 \times 10^9 \exp[-(8.50 \pm 0.40/RT)]$. In the case of methane, the activation energy was evaluated experimentally to be larger than 10 kcal mol^{-1}. Activation energies were calculated using the method proposed by Zavitsas. Calculated and experimental values are in good agreement, the calculated one for methane being 10.0 kcal mol^{-1}. A tentative Arrhenius expression for this compound is $5\ (\pm 2) \times 10^8 \exp[-(10.5 \pm 0.5/RT)]\ M^{-1}\ s^{-1}$. The activation energies determined in this work are consistent with a value of the bond dissociation energy $D(H_2N{-}H)$ in ammonia equal to 105 ± 1 kcal mol^{-1}. The results indicate that hydrogen abstraction by NH_2 essentially takes place on the most substituted carbon atom of the alkane: more than 90% on the tertiary position of isobutane, and 89 and 80% on the secondary positions of *n*-butane and propane, respectively. When compared to other radicals, the reactivity of NH_2 with respect to hydrogen abstraction reactions is intermediate between those of isoelectronic OH and CH_3 radicals.

Introduction

Hydrogen atom transfer reactions have been studied extensively[1] during the past 20 years and they have been invoked in many mechanisms. The ability of an odd-electron species to undergo hydrogen-abstraction reactions is considered to be one of its fundamental properties.

Theoretical chemists have also been interested in these processes, and activation energies have been successfully predicted by fairly simple semiempirical calculations.[2-4]

As we emphasized in a recent paper,[5] the reactivity of the NH_2 radical has been, so far, largely ignored, despite the fact that this radical is a key intermediate in most chemical transformations of ammonia in the gas phase. Kinetic data are needed for the reactions of ammonia with hydrocarbons.

The lack of this data is one of the principal reasons for the difficulties in interpreting many chemical systems involving this radical, particularly the experiments performed some years ago, aimed at simulating primary atmospheric chemistry.

Subsequent to our study of the addition reaction of NH_2 to olefins,[5] we examined the hydrogen-abstraction reaction of NH_2 with a series of alkanes. Absolute rate constants for the hydrogen abstraction from ethane, propane, butanes, and molecular hydrogen have been determined over the temperature range 300–520 K. Measurements were performed using flash photolysis in conjunction with a laser resonance absorption detection of NH_2 radicals. This technique provides the very high detection sensitivity necessary for measurement of low reaction rates, independently of pressure. In the case of methane, however, the reaction is so slow that the rate parameters could not be measured. In addition, activation energies have been estimated for each reaction, using the semiempirical method proposed by Zavitzas,[3] and compared to the corresponding experimental values.

Relatively little has been reported about hydrogen-abstraction reactions by NH_2. In a study of the photolysis of isobutane–ammonia mixtures, it was shown that the NH_2 radical abstracted hydrogen from isobutane, and a rate constant of the order of $10^4\ M^{-1}\ s^{-1}$ at room temperature could be evaluated.[6] Hydrogen-abstraction reactions were also suggested to occur in the photolysis of NH_3–propane mixtures[7] and of HNCO vapor in the presence of paraffins.[8] In the particular case of methane, the Arrhenius factors ($A = 8.5\ M^{-1}\ s^{-1}$; $E = 11.8$ kcal mol^{-1}) could be calculated from the rate parameters of the reverse reaction and the equilibrium constant obtained from thermodynamic data.[9] It should be also mentioned that the abstraction of the allyl hydrogen atoms by NH_2 may also occur in certain olefins.[5]

Experimental Section

The flash photolysis apparatus, equipped for laser resonance absorption detection of NH_2 radicals, has been described in preceding papers.[5,10] NH_2 radicals are produced by photolysis of ammonia through ordinary quartz using two argon-filled flash lamps, dissipating 5–30 J of electrical energy in about 20 μs. NH_2 radicals are obtained mainly in their ground electronic and vibrational state[11] and, if a few radicals may be formed in the excited state, as recently proposed,[12] they undergo a very fast collision quenching owing to the high pressures used in the present study.

The NH_2 concentration is monitored as a function of time by resonance absorption, using a single mode CW dye laser (Spectra Physics 580) tuned onto the strong NH_2 absorption line at 597.93 nm (0, 9, 0 ← 0, 0, 0 vibronic band). 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. Absorptions are always measured at the maximum of the line, resulting in a high radical detection sensitivity. As will be shown further on, the measurement of low reaction rates, which is the case in this work, necessitates that the experiments be carried out with the lowest possible radical concentration. Therefore the radical detection sensitivity must be as high as possible and independent of the sample pressure. These requirements are satisfied in the case of the laser resonance absorption since the broadening of the line with pressure causes no more than a threefold decrease in sensitivity over the pressures we examined.

Furthermore, we improved our sensitivity by using a long optical path length (generally 28 m, obtained in a multipass system) and by accumulating up to 200 decay curves in a signal averager. This system allowed us to record the decay of NH_2 following the flash, with an initial absorption smaller than 1%. This corresponds to an initial NH_2 concentration of about 2×10^{-10} mol L^{-1} at atmospheric pressure. For such low concentration and in the absence of reactions other than NH_2 recombination, the NH_2 radical can be observed for more than 100 ms. This long lifetime allows the measurement of very small reaction rate constants, the lowest limit being 10^3–$10^4\ M^{-1}\ s^{-1}$.

Activation energies were measured by enclosing both the flash lamp

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and the reaction cell in a furnace which could be heated up 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. Ethane, propane, and butanes (all 99.95%) were degassed at low temperature and used without further purification. Methane (99.995%) and hydrogen (99.995%) were used directly from the cylinder. The absence of degassing for these two gases should not be critical since it has been shown that NH_2 does not react with oxygen.[13] According to the manufacturer (L'Air Liquide) the residual impurities in ethane, propane, and butanes are essentially other alkanes which react similarly to the principal compound. This has been verified in the case of isobutane, in which only negligible traces of isobutene could be detected by gas chromatography.

Results and Discussion

The photodissociation of ammonia at wavelengths longer than 180 nm is now well established:

$$NH_3 \xrightarrow[\lambda > 180\ \text{nm}]{h\nu} NH_2(^2B) + H \qquad (1)$$

In the presence of an alkane, the NH_2 radical has been shown to react by hydrogen abstraction.[6] This result was confirmed by irradiating ammonia at 206.2 nm, using an iodine lamp, in the presence of a large excess of isobutane (NH_3, 1 Torr; $i\text{-}C_4H_{10}$, 200 Torr). Molecular hydrogen is formed with a quantum yield close to one and no ammonia disappears, as shown by its UV absorption at 213 nm. The same result is obtained by substituting ethane (500 Torr) for isobutane. In similar conditions, NH_3 disappears with a quantum yield of 0.8 ± 0.2 in the presence of ethylene (100 Torr) since NH_2 reacts in this case by addition to the double bond.[5]

At lower pressure of isobutane (100 Torr) and higher pressure of ammonia (40 Torr), which decrease the effective volume of irradiation and increase the radical concentration, radical recombinations can take place and *tert*-butylamine and hydrazine are found in the products along with octanes and isobutene.[6]

The dissociation of ammonia initiates the following radical reactions, if RH is an alkane:

$$H + RH \rightarrow H_2 + R \qquad (2)$$

$$NH_2 + RH \rightarrow NH_3 + R \qquad (3)$$

$$H + NH_2 + M \rightarrow NH_3 + M \qquad (4)$$

$$NH_2 + NH_2 + M \rightarrow N_2H_4 + M \qquad (5)$$

$$\left.\begin{array}{r} H + R \rightarrow \\ NH_2 + R \rightarrow \\ R + R \rightarrow \end{array}\right\} \begin{array}{l}\text{addition +}\\ \text{disproportionation}\end{array} \qquad \begin{array}{c}(6)\\(7)\\(8)\end{array}$$

According to this mechanism, the decay of NH_2 after the flash can be expressed as

$$-d[NH_2]/dt = k_3[NH_2][RH] + k_4[H][NH_2] + 2k_5[NH_2]^2 + k_7[NH_2][R] \qquad (9)$$

the initial concentration of NH_2 and H being equal.

Since reactions 4 and 5 are termolecular, the bimolecular rate constants k_4 and k_5 are pressure dependent. k_4 was shown to be sufficiently small at pressures lower than 1000 Torr[14] that reaction 4 is much slower than reaction 2 and can be neglected in this system. The recombination rate constants k_5 and k_7 have been measured in our laboratory. The value of k_5 is also pressure dependent up to several hundred Torr. Its value at the high-pressure limit is[15] $k_5(\infty) = 1.5 \times 10^{10}\ M^{-1}\ s^{-1}$. k_7 was measured by flashing ammonia in the presence of low pressure of olefins (0.1-0.3 Torr) so that the addition of H atoms to the double bond yielded rapidly an alkyl radical and reaction 7 was the principal recombination process of NH_2: $k_7 = 1.5\text{-}2.5 \times 10^{10}\ M^{-1}\ s^{-1}$ for ethyl, isopropyl, and *tert*-butyl radicals at room temperature.[16]

The values of k_3 measured in this work are generally five to six orders of magnitude smaller than the radical recombination rate constants k_5 and k_7. Therefore, much care must be taken to set the experimental conditions in order that reaction 3 is the principal reaction path of NH_2. Accurate determination of k_3 can be obtained only if the NH_2 decay is pseudo first order and therefore the initial radical concentration must be as small as possible so that all the radical recombinations are negligible compared to reaction 3. If this is not the case, the determination of k_3 necessitates the simulation of complex decay kinetics with the knowledge of the initial radical concentrations and of the rate-constant values at different temperatures and pressures. These are not known with sufficient confidence.

It was assumed that the NH_2 decay was pseudo first order if the rate of reaction of NH_2 with the alkane was at least one order of magnitude faster than its rate of reaction with radicals. After having evaluated the Arrhenius parameters of k_3 in preliminary experiments, we could then calculate for each experiment the maximum initial NH_2 concentration (or absorption) which fulfilled the above condition. From eq 9, this condition can be expressed as

$$k_3[RH] > 10(3k_R[NH_2]_0) \qquad (10)$$

assuming that $k_5 \simeq k_7 = k_R$ and that the initial concentrations $[NH_2]_0 \simeq [R]_0$. Then

$$[NH_2]_0 < k_3[RH]/30k_R \qquad (11)$$

k_R was taken equal to $2 \times 10^{10}\ M^{-1}\ s^{-1}$. It should be noted that the approximations generally tend to increase the factor of 10 in eq 10 by an additional factor of about 2.

The highest pressure of alkane used was 600 Torr at room temperature, which corresponds to 1000 Torr at 500 K. This was the maximum pressure that the reaction cell could support.

If NH_2 reacts only with alkane molecules, its pseudo-first-order decay rate should be independent of the initial concentration of the radical. This was verified by varying the intensity of the flashes. No deviations larger than experimental errors could be detected when relation 11 was obeyed.

Except for isobutane, however, these conditions were never fulfilled at room temperature for the other alkanes. For methane, over the whole range of temperatures 300-520 K, these conditions could not be met; therefore no precise experimental parameters for the reaction of NH_2 with CH_4 can be given here. We suspect, however, that the lowest values of k_3 obtained around 500 K for CH_4 are probably close to the true values (see discussion on CH_4).

A pseudo-first-order decay of NH_2 is shown in Figure 1 for the case of isobutane at 407 K. In the case of very low absorptions, when the signal to noise ratio was small, we could not always determine whether the decay was strictly first order. The decay was then assumed to be first order if radical recombinations could be neglected as described above. If no reaction occurred with the alkane, the NH_2 decay rate, only due to radical recombination, would be between 10 and 100 times longer than that generally measured.

The first-order decay rate of NH_2 was measured as a function of the alkane pressure. As expected, good linear dependences were obtained as shown in Figures 2a and 2b in the cases of ethane and hydrogen at 463 K and isobutane and propane at 373 K. This shows again that NH_2 only reacts with the alkane. An alternate explanation of such a result might be a direct photolysis of the alkane. Alkanes, however, do not decompose when irradiated through ordinary quartz. In ad-

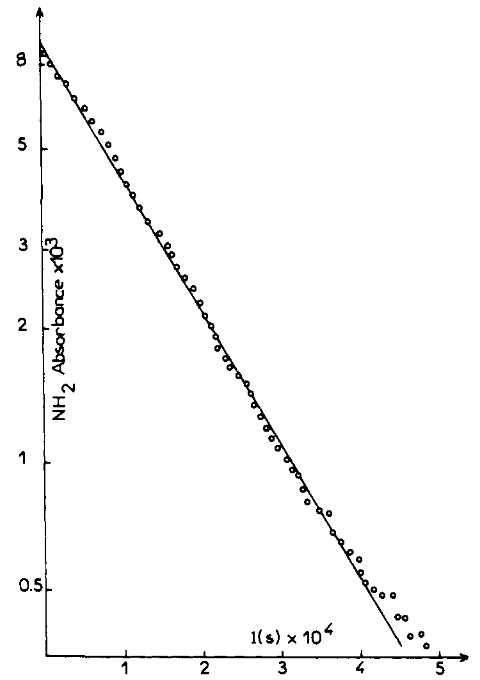

Figure 1. Semilogarithmic plot of the NH_2 absorbance decay against time at 397 K, NH_3 = 3 Torr, *i*-C_4H_{10} = 400 Torr. Under these conditions, the NH_2 extinction coefficient at the maximum of the line is 3500 ± 500 M^{-1} cm^{-1}, resulting in an initial NH_2 concentration of 8.5×10^{-10} M.

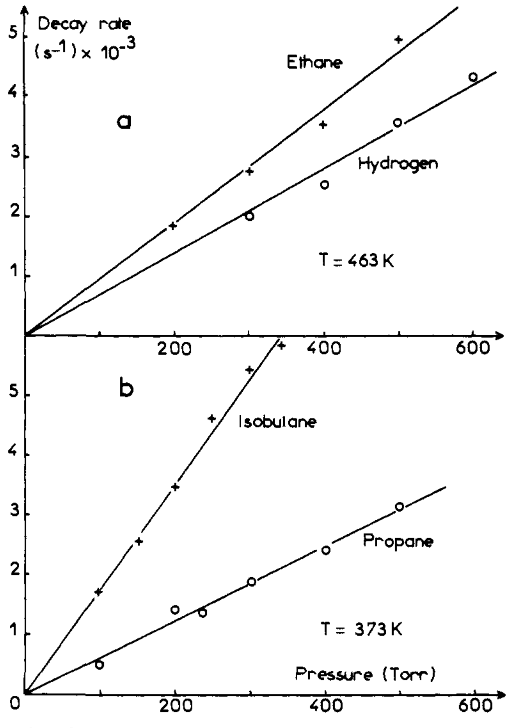

Figure 2. Plot of the pseudo-first-order decay rate of NH_2 against alkane (and hydrogen) pressure for (a) ethane and hydrogen at 463 K and (b) propane and isobutane at 373 K. The ammonia pressure was 3 Torr and no diluent gas was added.

dition, direct alkane photolysis would have resulted in a linear dependence of the pseudo-first-order decay rate on the flash intensity.

The temperature dependence of k_3 was studied from room temperature up to 520 K. However, a lowest temperature of investigation had to be determined as indicated above in order to obey relation 11. These temperatures were about 300 K for isobutane, 330 K for *n*-butane and propane, 360 K for ethane, and 400 K for hydrogen. For each compound, k_3 was measured

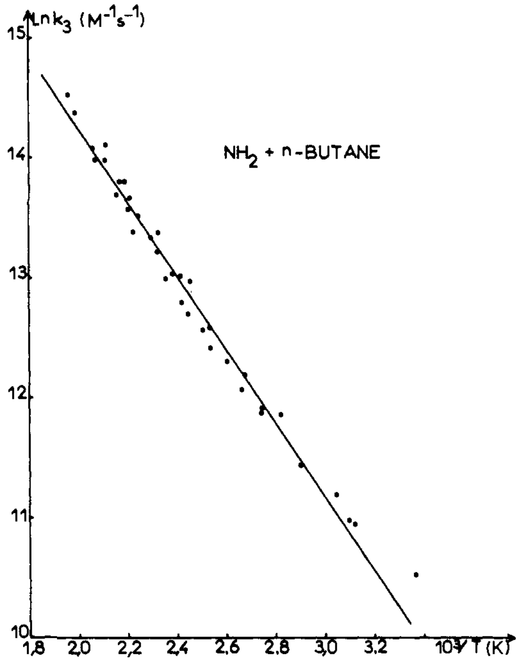

Figure 3. Arrhenius plot of ln k_3 against $1000/T$ for *n*-butane.

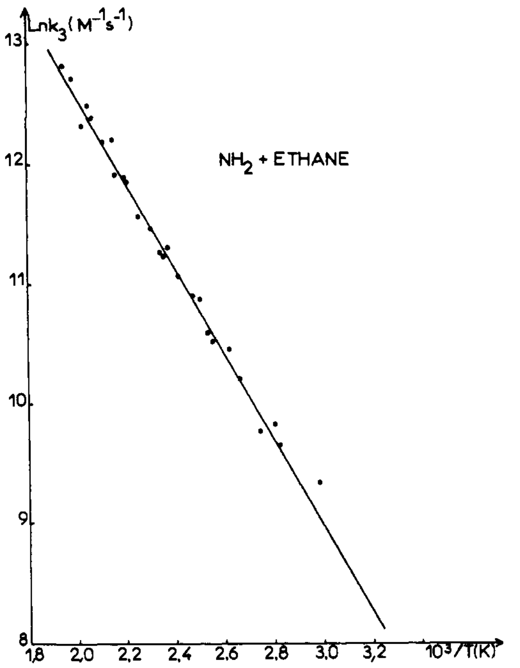

Figure 4. Arrhenius plot of ln k_3 against $1000/T$ for ethane.

at four to six different pressures and five to eight different temperatures. Each value of k_3 was determined from the accumulation of 100 200 decays.

As expected, significant activation energies were observed for the hydrogen abstraction from alkane and molecular hydrogen by NH_2. This is shown by the Arrhenius plots given in Figures 3-5 in the case of *n*-butane, ethane, and hydrogen. Similar plots were obtained with other compounds. These give reasonable straight lines, indicating that there is no change in the activation energy in the range of temperature examined.

The Arrhenius parameters were deduced from least-squares treatments of the experimental data. They are given in Table I. Rate constants calculated at room temperature are also presented. These give a good indication of the relative reactivity of NH_2 toward the different compounds.

As was expected from a preceding work,[6] the reactivity of

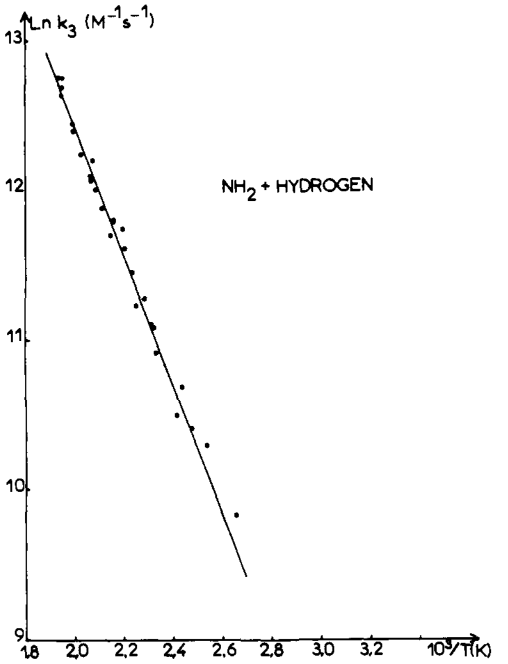

Figure 5. Arrhenius plot of ln k_3 against $1000/T$ for hydrogen.

NH_2 toward alkanes is rather low, particularly at room temperature. However, owing to the significant activation energies of these reactions, the reactivity increases rapidly as the temperature is raised. The difference in reactivity among the various compounds essentially arises from the differences in the activation energies, which vary from about 5 kcal mol^{-1} for isobutane to probably more than 10 kcal mol^{-1} in the case of methane.

The preexponential factors are similar for all the compounds but significantly higher for molecular hydrogen. This is generally observed in the case of hydrogen-abstraction reaction by other radicals.[1] However, in the case of alkanes, the preexponential factors have a slight tendency to increase with the number of active hydrogen atoms (with the exception of ethane) even though these variations are hardly larger than the experimental uncertainties.

It is generally observed that the activation energy of an hydrogen abstraction reaction by a given species increases with the energy D(C–H) of the C–H bond broken. This is also the case for the reaction of NH_2 with the series of alkanes we studied, as shown in Table I in which are included the corresponding C–H bond energies of the most active hydrogen atom in each molecule.

Evans and Polanyi[17] derived an empirical linear relation between the activation energy E and the enthalpy of the reaction ΔH, for a series of related reactions:

$$E = \alpha \Delta H + C \tag{12}$$

α and C are constants.

For a unique attacking species X, the same X–H bond is formed in all reactions and ΔH can be replaced by the energy of the C–H bond which is broken:

$$E = \alpha[D(\text{C–H}) + C'] \tag{13}$$

This equation, generally referred to as the Polanyi relation, has been shown to be verified for many atoms or radicals,[1] especially in the case of the same series of alkane as the one we have studied. This is shown in Figure 6, in the particular cases of OH and CH_3 radicals. For NH_2, the points corresponding to the three activation energies determined in this work for the abstraction of tertiary, secondary, and primary C–H bonds are also correlated. The extrapolation to the D(C–H) value of methane would yield an activation energy slightly smaller than 10 kcal mol^{-1}.

Table I. Experimental Arrhenius Parameters for Reaction 3 and k_3 Values at Room Temperature[a]

	$10^{-8}A$, $M^{-1}s^{-1}$	E_a, kcal mol^{-1}	$10^{-4}k_3$, $M^{-1}s^{-1}$ (300 K)	lowest D(C–H), kcal mol^{-1}
hydrogen	12.6	8.50 ± 0.40	0.087	104.2
methane		>10		104.8
ethane	3.7	7.15 ± 0.28	0.26	98
propane	4.5	6.15 ± 0.25	1.60	94.5
n-butane	7.0	6.10 ± 0.25	2.60	94.5
isobutane	2.3	4.90 ± 0.22	6.42	91

[a] The C–H bond energy D(C–H) of the most active hydrogen atom is also indicated.

It has been shown recently that activation energies of hydrogen-abstraction reactions can be calculated by simple semiempirical methods.[3,4] These methods have given fairly good results for many types of reactions.

We found it of interest to calculate the activation energies, using one of these methods, and compare the results with the experimental values. We chose Zavitsas' method[3] in which the total energy $E^{\ddagger}_{tot}$ of the transition state is expressed as

$$E^{\ddagger}_{tot} = E^{\ddagger}_{RH} + E^{\ddagger}_{R} + E^{\ddagger}_{RN} \tag{14}$$

corresponding to the linear transition state

$$R\text{- -}H\text{- -}NH_2$$

$E^{\ddagger}_{RH}$ is the R- -H bond energy in the transition state, assumed equal to that of the H- -NH_2 bond, and determined from the Morse equation;[3] $E^{\ddagger}_{R}$ is the resonance energy estimated from that of allyl radical and taken equal to 10.6 kcal mol^{-1}; $E^{\ddagger}_{RN}$ is the repulsion energy between R and NH_2, as determined from the Sato equation.[3]

The value of $E^{\ddagger}_{tot}$ is determined from the minimum value of eq 14 as the R- -H distance is varied.

The calculated activation energies are given in Table II and compared to the experimental results. The parameters used in the calculations are also included in this table. The value of D(N–H) in ammonia was the one proposed by Zavitsas:[3] 105 kcal mol^{-1}. It has already given satisfactory results in this type of calculations,[3] and furthermore it is consistent with our experimental results, as shown further on.

The calculated values are in fairly good agreement with the experimental results except in the cases of hydrogen and ethane, for which one finds a difference of about 1 kcal mol^{-1}. In the case of ethane, the calculated activation energy is obviously too small since it is about the same as the one calculated for the abstraction of the secondary hydrogen in propane. However, the differences observed are in the range of the calculations' uncertainties. They are probably due to an uncertainty in the values of D(R–N) and w_0(R–N) in the corresponding amines. Nevertheless, the agreement is quite satisfactory since, on one hand, it substantiates the experimental results obtained in this work and, on the other hand, it allows the calculation of activation energies for the reaction with other alkanes with good confidence.

This is particularly true for the case of methane since the reaction was too slow for us to be able to determine experimentally the Arrhenius parameters. Some measurements could be performed, however, at high temperature and the results are consistent with the calculated value of 10.0 kcal mol^{-1}. Indeed, assuming a preexponential factor of 5×10^8 $M^{-1}s^{-1}$, similar to those obtained for other compounds, the lowest values of k_3 (CH_4) measured between 480 and 520 K give an activation energy of 10.3 kcal mol^{-1}. However, the extrapo-

Table II. Parameter Values Used in Activation Energies Calculations and Comparison of Calculated and Experimental Results[a]

R- -H- -NH_2	ω_0(R-H), cm^{-1}	r_e(R-H), Å	D(R-N), kcal mol^{-1}	ω_0(R-N), cm^{-1}	r_e(R-N), Å	E_a, kcal mol^{-1} calcd	E_a, kcal mol^{-1} exptl
$(CH_3)_3C$- -H- -NH_2	2890	1.09	81	1033	1.48	5.21	4.90
$(CH_3)_2CH$- -H- -NH_2	2890	1.09	81	1040	1.48	6.00	6.15
C_2H_5- -H- -NH_2	2952	1.09	81	1079	1.48	6.13	7.15
CH_3- -H- -NH_2	2967	1.09	82	1044	1.48	10.01	>10
H- -H- -NH_2	4395.2	0.742	105	3390	1.01	7.62	8.5
ref	18	18	*b*	20	20		

[a] ω_0 = equilibrium vibrational frequency; r_e = equilibrium internuclear distance; D(R-N) = R-N bond energy in the corresponding amine. [b] D(R-N) in methylamine was calculated taking $D(H_2N-H)$ = 105 kcal mol^{-1} and $\Delta H_f°(CH_3NH_2) = -5.5$ kcal mol^{-1}. D(R-N) values for other amines were taken 1 kcal mol^{-1} smaller than in methylamine, according to ref 19.

lated value of 9.5 kcal mol^{-1} from the data plotted in Figure 6 seems too small since, if it were true, its experimental determination would have been possible.

On the contrary, the value of 11.8 kcal mol^{-1} determined by Gray et al.[9] from the reverse reaction is certainly too high since, despite the bad reproducibility of our measurements between 480 and 520 K (probably owing to the occurrence of radical recombinations), an apparent activation energy of about 10 kcal mol^{-1} could be evaluated. If the real activation energy were higher than 11.5 kcal mol^{-1}, the rate constant for hydrogen abstraction from methane at 500 K would have been much smaller than the one we have actually measured. This means that in our experiments the participation of the NH_2 recombination with radicals would have been so important that the apparent activation energy would have been much smaller than the measured 10 kcal mol^{-1} (<5 kcal mol^{-1}, assuming that radical recombinations occur without activation energy). This is a good indication that the measured rate constants in this range of temperature should be close to the actual values and that the activation energy for hydrogen abstraction from methane should not be higher than 11 kcal mol^{-1}. Furthermore, Gray et al.[9] determined their value by using the bond dissociation energy $D(H_2N-H)$ = 102.5 kcal mol^{-1}, which was found subsequently to be too low. Benson[19] proposed 109 kcal mol^{-1} and Zavitsas[18] 105 kcal mol^{-1}. These values would result, taking $D(H_3C-H)$ = 104.8 kcal mol^{-1}, in activation energies of 6.1 and 10.1 kcal mol^{-1}, respectively, instead of 11.8 determined by Gray et al.[9] Obviously the value $D(H_2N-H)$ = 105 kcal mol^{-1} is the most consistent with the present results. Finally, the Arrhenius parameters for the reaction of NH_2 with methane can be estimated with a fair degree of confidence as $A = 5\ (\pm 2) \times 10^8\ M^{-1}\ s^{-1}$ for the preexponential factor and $E_a = 10.5\ (\pm 0.5)$ kcal mol^{-1} for the activation energy.

This work can provide important information concerning the N-H bond dissociation energy of ammonia which is not yet known accurately. The activation energy of the reverse reaction

$$CH_3 + NH_3 \rightarrow CH_4 + NH_2 \qquad (15)$$

has been determined experimentally to be $E_a' = 10\ (\pm 0.3)$ kcal mol^{-1} (see ref 9). Accepting E_a = 10.5 kcal mol^{-1} for the forward reaction as determined here above, the bond energy D(N-H) in ammonia is about 0.5 kcal mol^{-1} smaller than the value of D(C-H) in methane, i.e., 104.3 kcal mol^{-1}.

A similar conclusion is obtained in the case of the NH_2 reaction with molecular hydrogen since the activation energies for both the forward and reverse reactions are known: 8.5 kcal mol^{-1} for the forward reaction determined in this work and 10 (±1.5) kcal mol^{-1} for the reverse reaction.[21] In this case, the bond energy $D(H_2N-H)$ is about 1.5 kcal mol^{-1} higher than D(H-H) in H_2, i.e., 105.7 kcal mol^{-1}. This value is in fairly good agreement with the one determined in the case of the reaction of NH_2 with methane and therefore we can propose D(N-H) = 105 (±1) kcal mol^{-1} for the bond dissociation energy in ammonia. This is in agreement with the value proposed by Zavitsas[3,18] deduced from calculations.

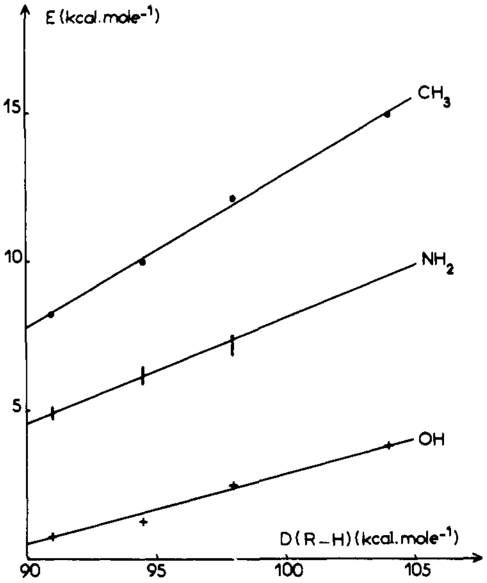

Figure 6. Plots of activation energies for hydrogen abstraction from alkanes against the bond energy D(R-H) for OH, NH_2, and CH_3 radicals. Data for OH and CH_3 are from ref 1.

In our calculations of activation energies, it is assumed that the site of hydrogen abstraction in the alkane molecule is the one corresponding to the lowest C-H bond energy, i.e., the tertiary position in isobutane and the secondary ones in *n*-butane and propane. It was actually shown that the yield of *tert*-butyl radical was about ten times greater than that of isobutyl radical in the reaction of NH_2 with isobutane.[6] It is generally admitted that the C-H bond energy of primary hydrogen atoms is about the same in all alkanes, except methane. This would result in a similar rate constant for the abstraction of any primary hydrogen atoms and this rate constant should be the one measured with ethane, taking into account the number of primary hydrogen atoms in each molecule. With this assumption, the relative rate constants can be calculated for the abstraction on the different positions of a given molecule:

$$k_{t(\text{or sec})}/k_p = (k_3 - k_p)/k_p \qquad (16)$$

with

$$k_p = k_3(C_2H_6)n(H_p)/6 \qquad (17)$$

k_p, k_{sec}, and k_t are the rate constants of abstraction on the primary, secondary, and tertiary positions, respectively; $n(H_p)$ is the number of primary hydrogen atoms in the molecule.

From the rate constants at room temperature given in Table I, the ratio of eq 16 is found equal to 15 for isobutane, 9 for *n*-butane, and 5 for propane. Taking into account the limited

Table III. Comparison of Arrhenius Parameters and Room Temperature Rate Constants for the Hydrogen-Abstraction Reaction by OH, NH_2, and CH_3 from Ethane, Propane, and Isobutane[a]

	log *A*, $M^{-1}\,s^{-1}$	*E*, kcal mol^{-1}	log *k*(300 K), $M^{-1}\,s^{-1}$
		Ethane	
OH	10.05	2.5	8.23
NH_2	8.6	7.15	3.42
CH_3	9.3	12.1	0.53
		Propane	
OH	9.85	1.3	8.90
NH_2	8.65	6.15	4.20
CH_3	8.85	11.6	0.45
		Isobutane	
OH	9.7	0.77	9.13
NH_2	8.4	4.9	4.85
CH_3	8.5	8.2	2.56

[a] Data for OH and CH_3 are from ref 1.

accuracy of the experimental determination yielding the ratio of 10 in the case of isobutane[6] and the approximations made in the above calculation, the agreement is acceptable. Note that the value calculated for *n*-butane is about twice that of propane, which is the same ratio as the number of secondary hydrogen atoms.

As expected, hydrogen abstraction takes place essentially on tertiary or secondary positions of the molecule. This is consistent with the good agreement between the overall activation energies determined experimentally and those calculated for a specific C–H bond. It also explains the good linearity of the Arrhenius plots since essentially a single activation energy is involved in the reaction. Even in the case of propane, where the abstraction on the primary position is significant, it is not large enough to cause a curvature of the Arrhenius plot (the activation energies measured for primary and secondary hydrogen atoms are moreover not much different).

Finally, it is interesting to compare NH_2 radicals with other radicals, particularly the isoelectronic OH and CH_3 species, in hydrogen-abstraction reactions.

Large differences in reactivity are observed between these three radicals, the reactivity of NH_2 being intermediate between those of OH and CH_3. This is shown in Table III, in which are compared the Arrhenius parameters and the rate constants at room temperature in the cases of ethane, propane, and isobutane. The difference of reactivity from one radical to other is essentially due to the large difference in the activation energies as also shown in Figure 6. The preexponential factors are similar for NH_2 and CH_3 (though slightly higher for CH_3 but perhaps not significantly). However, they are generally an order of magnitude higher for OH, which results in a very high reactivity for this radical.

The behavior found for NH_2, in the compared reactivity with OH and CH_3, is similar in both hydrogen abstraction and addition to a double bond.[5]

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Electrolytes. From Dilute Solutions to Fused Salts

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Abstract: Solutions with composition extending continuously from molecular liquids such as water to fused salts are relatively unusual but of considerable interest. Conductance and thermodynamic properties are considered for several examples. New equations for the activities of the respective components represent the data more accurately than previous treatments and delineate the similarities and differences between such systems and nonelectrolyte solutions.

Electrolyte systems extending in the liquid phase from a dilute solution in a polar molecular solvent (such as water or an alcohol) to a pure fused salt constitute an interesting but infrequently studied type. In a 1954 article with the same title as this paper, Kraus[1] summarized the information then available concerning such systems. Kraus emphasized measurements of conductance but also considered the few thermodynamic data then available for such systems. In the following 25 years, the vapor pressure and thereby the activity of water have been measured for the systems $(Li,K)NO_3$–H_2O and $(Ag,Tl)NO_3$–H_2O over the entire range from pure water to fused salt. In each case there is a fixed, nearly equal ion

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