THE KINETICS OF THE GAS PHASE REACTIONS OF NH$_2$ RADICALS WITH ALKANE AND ALKYL RADICALS
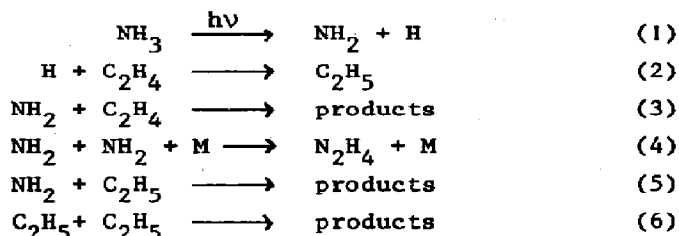
R. Lesclaux and M. Demissy

Laboratoire de Chimie Physique A, Université de Bordeaux I, 33 405 Talence (France)

The amino radical is an important species in all chemical processes involving ammonia. The knowledge of the reactivity of this radical is important either in the field of atmospheric chemistry or in general fundamental chemistry. Preceding works reported the kinetics of the reactions of NH$_2$ with NO (1), O$_2$(2), olefins (3), and the recombination NH$_2$ + NH$_2$ (4). In the particular case of olefins, it was found that the Arrhenius parameters are similar for all the compounds studied : ethylene, propylene and butene isomers (A $\simeq$ 1-3 x 10^8 M^{-1}s^{-1} and E = 4 Kcal mole^{-1}) and the addition of NH$_2$ to the double bond was shown to be the principal process.
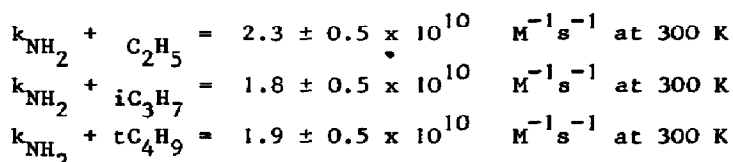
In this work, absolute rate constants are reported for the recombination reaction of NH$_2$ with alkyl radicals and for the hydrogen abstraction reactions from alkanes and molecular hydrogen in the temperature range 295-500K. Decay rates are measured by flash photolysis, using a laser resonance absorption detection of the radicals.

The experimental set up was described in preceding papers (1,3). NH$_2$ is produced by flash photolysis of ammonia through ordinary quartz and its concentration is monitored by absorption spectrometry using a laser tuned on a NH$_2$ absorption line. The laser is a single mode CW dye laser Spectra Physics 580. The signal from generally 100 flashes are accumulated in a signal averager. The decay kinetics are measured with initial concentration of about 3 x 10^{11} molecules.cm^{-3}.

By flashing ammonia in the presence of an olefin, the following reactions take place in the cell in the particular case of ethylene :

$$NH_3 \xrightarrow{h\nu} NH_2 + H \qquad (1)$$

$$H + C_2H_4 \longrightarrow C_2H_5 \qquad (2)$$

$$NH_2 + C_2H_4 \longrightarrow products \qquad (3)$$

$$NH_2 + NH_2 + M \longrightarrow N_2H_4 + M \qquad (4)$$

$$NH_2 + C_2H_5 \longrightarrow products \qquad (5)$$

$$C_2H_5 + C_2H_5 \longrightarrow products \qquad (6)$$

If the olefin pressure is 0.1 to 0.3 Torr, reaction 2 is fast, reaction 3 is slow ($k_3 \sim 10^5 M^{-1}s^{-1}$) and reaction 4 is also slow because of the low total pressure (2 - 3 Torr). Thus, the principal disappearance channel of NH_2 is reaction 5. k_5 can then be determined by computer simulation of the NH_2 decay kinetics, all the other rate constants being known. The initial concentration of NH_2 is measured by a method already described (4). Using ethylene, propylene and isobutene, k_5 has been determined for ethyl, isopropyl and t-butyl radicals :

$$k_{NH_2 + C_2H_5} = 2.3 \pm 0.5 \times 10^{10} \quad M^{-1}s^{-1} \text{ at } 300 \text{ K}$$

$$k_{NH_2 + iC_3H_7} = 1.8 \pm 0.5 \times 10^{10} \quad M^{-1}s^{-1} \text{ at } 300 \text{ K}$$

$$k_{NH_2 + tC_4H_9} = 1.9 \pm 0.5 \times 10^{10} \quad M^{-1}s^{-1} \text{ at } 300 \text{ K}$$

A part of the incertitude arises from the fact that different values for k_6 can be found in the literature.

If an alkane replaces the olefin, the same reactions occur, reaction 2 and 3 becoming in this case hydrogen abstraction reactions.

$$NH_2 + C_nH_{2n+2} \longrightarrow NH_3 + C_nH_{2n+1} \qquad (7)$$

Reaction 7 is generally very slow compared to recombination reactions 4 and 5. Measurements of k_7 require therefore very low initial radical concentrations in order to neglect the participation of reactions 4 and 5. This condition could not be achieved in the case of methane, even at a pressure of 600 Torr.

The Arrhenius parameters obtained for a series of alkanes are the followings :

	$10^{-8}A$ ($M^{-1}s^{-1}$)	E (kcal.mole^{-1})		$10^{-4}k_7$ ($M^{-1}s^{-1}$)
		Experimental	calculated	300 K
Isobutane	2.3	4.9 ± 0.22	5.26	6.4
n-butane	7.0	6.1 ± 0.25	-	2.6
Propane	4.5	6.15 ± 0.25	6.07	1.6
Ethane	3.7	7.15 ± 0.28	7.01	0.26
Methane	-	-	11.50	-
Hydrogen	12.6	8.50 ± 0.40	7.88	0.087

The preexponential factors are about the same as those observed in similar reactions and as expected, the activation energies increase with the CH bond strength.

Activation energies were calculated using the method described by ZAVITSAS (5). The results are reported in the table above. In spite of the simplicity of the method a good correlation is obtained between calculated and experimental results. The value obtained with methane is 11.50 Kcal $mole^{-1}$, in agreement with the value calculated from the reverse reaction kinetic parameters : 11.8 kcal. $mole^{-1}$ (6). However these values seem high compared either to those obtained with hydrogen and ethane or to the experimental rate constants k_7 that could be measured at high temperatures, apparently in good conditions. Further measurements are in progress in order to clarify this point.

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