

B1

Flash Photolysis of Ketene: Reactions of Methylene Radicals

M. J. PILLING and J. A. ROBERTSON
Physical Chemistry Laboratory, South Parks Road, Oxford (U.K.)

Ketene was flash photolysed at wavelengths greater than 160 nm. The photolysis lamp was of a four electrode pair design, with Marx-Bank circuitry, operating at 1000 J with a $1/e$ decay time of $< 4 \mu\text{s}$. The photolysis products were analysed by gas chromatography. Experiments were mainly limited to studies of ketene with inert gases, hydrogen and methane, although the mixed photolysis system, ketene + azomethane, was also examined. The experimental results were compared with kinetic simulations based upon Merson's method of numerical integration of coupled differential equations. The program included a realistic simulation of the lamp profile, and varied the step length until the error in a single step was $< 10^{-4}\%$.

The major new result is the observation of "singlet" products, ethane and methane, at limiting high inert gas pressures, in mixtures containing low pressures of hydrogen. Various schemes are suggested to explain this result; the most satisfactory one implicates CH_2^1B_1 in the reaction system.

The rate constants for reaction of CH_2^3B_1 and CH_3 , and of CH_2^1A_1 and H_2 , CH_4 , C_2H_2 , CH_2CO , O_2 and CO are discussed. RRKM calculation for several radical-radical and radical-molecule reactions are presented.

B3

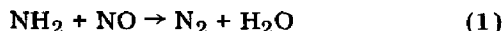
Flash Photolytic Studies of NH_2 Reaction Kinetics

R. LESCLAUX, PHAM VAN KHE, J. C. SOULIGNAC and J. JOUSSOT-DUBIEN
Université de Bordeaux I, Laboratoire de Chimie Physique A, 33405 Talence (France)

A better knowledge of the kinetics of NH_2 radical reactions would be of a great importance in the determination of the photochemical and chemical processes of ammonia in various systems, especially in the atmosphere. A flash photolysis apparatus was built for such a study. The particular specifications of the set up are described elsewhere [1].

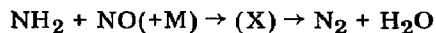
Preliminary experiments confirmed that NH_2 is a weakly reactive radical. No reaction ($k < 10^5 \text{ M}^{-1}\text{s}^{-1}$) was observed with O_2 , CO , N_2O , C_2H_2 , olefins, alkanes,...etc. at room temperature. Even at 500 K no reaction could be detected with oxygen.

A well known reaction of NH_2 is the reaction



This reaction is important since it corresponds to the elimination of nitrogen oxides. Its rate constant was determined only in very specific conditions [2, 3].

Our measurements at 300 K and at high pressure (700 Torr of N_2) give a value of $k_1 = 1.1 (\pm 0.2) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, in agreement with previous values. The question that has been raised is whether this reaction should be written



X being addition product of NH_2 and NO . In this case, the reaction should be termolecular. We have measured k_1 in a wide range of pressure, from 2 to 700 Torr with $\text{M} = \text{NH}_3$, N_2 , and SF_6 . No significant variation of k_1 could be detected in this pressure range. Reaction (1) must then be considered as being bimolecular at pressure higher than 2 Torr.

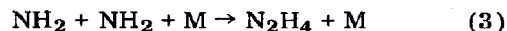
Small variations of k_1 were observed with temperature (20 to 240 °C), indicating a slight decrease of k_1 which corresponds to a negative activation energy of $1.05 \pm 0.2 \text{ kcal mole}^{-1}$.

NH_2 reacts rather slowly with olefins but we have been able to measure the rate constant of the reaction



in the temperature range 150 to 240 °C. The value obtained is $k_2 = 3 \times 10^9 \exp(-5.8 \pm 2/RT) \text{ M}^{-1}\text{s}^{-1}$ (E in kcal mole^{-1}) which is much lower than a previously proposed value [2]. Such a preexponential factor and activation energy are in agreement with an addition reaction.

The recombination reaction



is important since it competes often with other NH_2 reaction. It is then interesting to know the rate constant k_3 in various conditions.

The bimolecular rate constant is pressure dependent up to several hundred Torr. The termolecular rate constant was determined