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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 μs. 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.

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### Flash Photolytic Studies of NH_2 Reaction Kinetics

R. LESCLAUX, PHAM VAN KHE, J. C. SOULIGNAC and J. JOUSSOT-DUBIEN
Université de Bordeaux 1, 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 ($k < 10^5$ $M^{-1}s^{-1}$) 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

$$NH_2 + NO \rightarrow N_2 + H_2O \qquad (1)$$
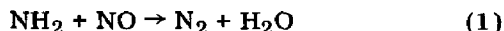
This reaction is important since it corresponds to the elimination of nitrogen oxides. Its rate constant was determined only in very specific conditions [2, 3].

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)$\times 10^{10}M^{-1}s^{-1}$, in agreement with previous values. The question that has been raised is whether this reaction should be written

$$NH_2 + NO(+M) \rightarrow (X) \rightarrow N_2 + H_2O$$
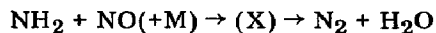
X being addition product of NH_2 and NO. In this case, the reaction should be thermolecular. We have measure k_1 in a wide range of pressure, from 2 to 700 Torr with M = NH_3, N_2, and SF_6. No significant variation of k_1 could be detected in this pressure range. Reaction (1) must then be considered 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 ± 0.2 kcal mole^{-1}.

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

$$NH_2 + C_3H_6 \rightarrow \text{products} \qquad (2)$$

in the temperature range 150 to 240 °C. The value obtained is $k_2 = 3 \times 10^9$ exp($- 5.8 \pm 2/RT)M^{-1}s^{-1}$ (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

$$NH_2 + NH_2 + M \rightarrow N_2H_4 + M \qquad (3)$$
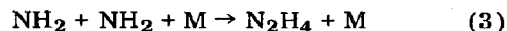
is important since it competes often with other NH_2 reaction. It is then interesting to know the rate constant k_3 in various conditions.

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

between 0.3 and 20 Torr for NH_3, N_2, and Ar as third bodies.

$$k_{NH_3}^{III} = 1.02 \times 10^{13} M^{-2} s^{-1}$$
$$k_{N_2}^{III} = 2.55 \times 10^{12} M^{-2} s^{-1}$$
$$k_{Ar}^{III} = 1.00 \times 10^{12} M^{-2} s^{-1}$$

A low pressure limit of 0.85 $M^{-1} s^{-1}$ was found for the bimolecular rate constant.

No temperature effect was found near the low pressure limit and a slight negative activation energy was measured for the thermolecular reaction at 20 Torr of nitrogen ($E = \sim - 1$ kcal mole^{-1}).

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2 S. Gordon, W. Mulhac, and P. Nangia, J. Phys. Chem., 75 (1971) 2087.
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B5
Primary Steps in the Photolysis of 1,1,2,2-Tetrachloroethane

T. YUAN and M. H. J. WIJNEN
Chemistry Department, Hunter College of the City University of New York, 695 Park Ave., New York, N.Y. 10021 (U.S.A.)

The photolysis of 1,1,2,2-tetrachloroethane has been investigated in the presence of I_2 as a function of the energy of the incident light and at various pressures of octafluorocyclobutane as inert deactivator.

The following reaction products were obtained: *cis*-1,2-$C_2H_2Cl_2$(33), *trans*-1,2-$C_2H_2Cl_2$(33), $CHCl_2CHClI$(13), C_2HCl_3(9), C_2Cl_4(7) and 1,1-$C_2H_2Cl_2$(4), where the numbers in parentheses are the relative yields at $\lambda > 3000$ A. The results indicate clearly that all three dichloroethylenes are produced from the same excited state and that these compounds in this wave length region are formed by molecular elimination of Cl_2.

The relative yield of $CHCl_2CHClI$ decreases sharply with decreasing wave length. The possibility that this may be caused by decomposition of excited $CHCl_2CHCl$ radicals is being studied.

A study of the primary process in the photolysis of 1,1,1-$C_2H_3Cl_3$ has been completed and the results of both investigations will be compared.

Some Recent High Resolution Spectroscopic Studies

D. A. RAMSAY
Division of Physics, National Research Council, Ottawa (Canada)

Topics which will be discussed include
1. The recognition of the phenomenon of axis-switching in the spectra of HCO and DCO which has yielded values for the A-rotational constants and has permitted a more accurate determination of the molecular geometry [1].
2. A reinvestigation of the near ultraviolet absorption bands of NCO [2].
3. The detection of a doublet–quartet perturbation in the violet system of CN [3].
4. The use of magnetic circular dichroism to investigate triplet states of molecules.

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3 J. A. Coxon, D. W. Setser and D. A. Ramsay, Can. J. Phys., in press.

C4
The Perturbation of Molecular Rydberg States

L. R. WILSON and S. LIPSKY
Department of Chemistry, University of Minnesota, Minneapolis, Minn. 55455 (U.S.A.)

Theoretical evidence for the existence of Rydberg/valence shell conjugate electronic states in polyatomic molecules has been reviewed recently by Robin [1]. In some cases, the relative importance of the Rydberg and valence shell configurations in the excited state wave function is predicted to vary with some parameter of the nuclear geometry as this alters in the course of the nuclear motion. Utilizing the higher sensitivity of the Rydberg configuration to external perturbation, we have sought experimental evidence for the existence of such states as manifested by the effect of high pressures of chemically inert gases to induce characteristic changes in the vibrational structure of the electronic absorption spectrum. In par-