

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

$$k_{\text{NH}_3}^{\text{III}} = 1.02 \times 10^{13} M^{-2} s^{-1}$$

$$k_{\text{N}_2}^{\text{III}} = 2.55 \times 10^{12} M^{-2} s^{-1}$$

$$k_{\text{Ar}}^{\text{III}} = 1.00 \times 10^{12} M^{-2} s^{-1}$$

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 thermal reaction at 20 Torr of nitrogen ($E = \sim -1 \text{ kcal mole}^{-1}$).

- 1 R. Lesclaux, Pham van Khe, P. Dezaudier and J. C. Soullignac, *Chem. Phys. Letters*, 1975, in press.
- 2 S. Gordon, W. Mulhac, and P. Nangia, *J. Phys. Chem.*, 75 (1971) 2087.
- 3 M. Gehring, K. Schacke and J. Wolfrum, Fourteenth Symposium (International) on combustion, The Combustion Institute, Pittsburgh, 1973, p. 99.

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Primary Steps in the Photolysis of 1,1,2,2-Tetrachloroethane

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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- $\text{C}_2\text{H}_2\text{Cl}_2$ (33), *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$ (33), CHCl_2CHCl (13), C_2HCl_3 (9), C_2Cl_4 (7) and 1,1- $\text{C}_2\text{H}_2\text{Cl}_2$ (4), where the numbers in parentheses are the relative yields at $\lambda > 3000 \text{ \AA}$. 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_2CHCl 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- $\text{C}_2\text{H}_3\text{Cl}_3$ has been completed and the results of both investigations will be compared.

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(Invited Lecture)

Some Recent High Resolution Spectroscopic Studies

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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.

- 1 J. M. Brown and D. A. Ramsay, *Can. J. Phys.*, in press.
- 2 P. S. H. Bolman, J. M. Brown, A. Carrington, I. Kopp and D. A. Ramsay, *Proc. Roy. Soc., London*, in press.
- 3 J. A. Coxon, D. W. Setser and D. A. Ramsay, *Can. J. Phys.*, in press.

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The Perturbation of Molecular Rydberg States

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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 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-