

between 0.3 and 20 Torr for  $\text{NH}_3$ ,  $\text{N}_2$ , 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.

### 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  $\text{I}_2$  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),  $\text{CHCl}_2\text{CHCl}$  (13),  $\text{C}_2\text{HCl}_3$  (9),  $\text{C}_2\text{Cl}_4$  (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  $\text{Cl}_2$ .

The relative yield of  $\text{CHCl}_2\text{CHCl}$  decreases sharply with decreasing wave length. The possibility that this may be caused by decomposition of excited  $\text{CHCl}_2\text{CHCl}$  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.

### C3

(Invited Lecture)

#### 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.

- 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.

### 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 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-

ticular we have examined the  $n_N \rightarrow 3s$  transitions of ammonia and some alkylated amines and the  $N \rightarrow V$  and  $N \rightarrow R$  transitions of ethylene and some of its alkylated derivatives using He, Ne, Ar,  $N_2$  and  $CF_4$  as perturbing gases.

- 1 M. B. Robin, *Higher Excited States of Polyatomic Molecules*, Vol. I, Academic Press, New York, 1974.

### C5

#### Excited Electronic States of $\alpha$ -, $\beta$ -, and $\gamma$ -Dicarbonyls

P. BRINT and S. P. McGLYNN

*Department of Chemistry, The Louisiana State University, Baton Rouge, La. 70803 (U.S.A.)*

The lower-energy  $^1\Gamma_{n\pi^*}$  states of dicarbonyls will be discussed on the basis of optical absorption, photoelectron spectroscopic and theoretical results. Examples of molecules which exhibit multiple  $^1\Gamma_{n\pi^*}$  excited states will be presented. Vacuum ultraviolet spectra of mono- and dicarbonyls will be presented and analysed, particular emphasis accruing to the utility of one- and two-chromophore models for the dicarbonyl Rydberg states.

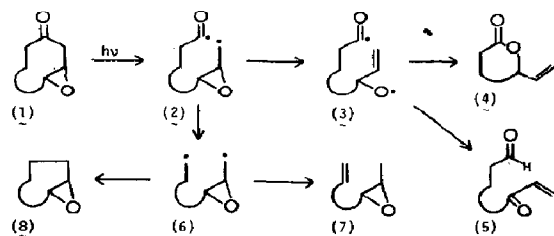
### E6

#### The Photochemistry of $\beta$ , $\gamma$ -Epoxy Cyclic Ketones

R. K. MURRAY, Jr., T. K. MORGAN, Jr., J. A. S. POLLEY, C. A. ANDRUSKIEWICZ, Jr., and D. L. GOFF

*Department of Chemistry, University of Delaware, Newark, Del. (U.S.A.)*

A general scheme is proposed to summarize the photochemistry of  $\beta$ ,  $\gamma$ -epoxy cyclic ketones. Irradiation of a  $\beta$ ,  $\gamma$ -epoxy cyclic ketone (1) initially leads to Norrish Type I bond cleavage and the formation of an apparent diradical species 2 which undergoes subsequent epoxide ring opening to give the acylalkoxy diradical 3. Unless specific sub-



stituent and/or skeletal constraints are present, product formation proceeds from 3 by competitive ring closure to give lactone 4 and hydrogen transfer to provide aldehyde 5. If the formation of either 4 or 5 is prevented, then the other product predominates. If the formation of both 4 and 5 is precluded, then decarbonylation occurs to give diradical 6 which undergoes disproportionation to provide 7 and/or ring closure to afford 8. Each of these possible contingencies has been examined experimentally.

### E7

#### Reactivity of Carbonyl $^1n, \pi^*$ States Toward Alkyl Amines

J. C. DALTON, J. J. SNYDER and M. C. GEIGER

*Department of Chemistry, University of Rochester, Rochester, N. Y. 14627 (U.S.A.)*

We have investigated the bimolecular reactivity of  $^1n, \pi^*$  states of eleven acyclic, cyclic and bicyclic alkyl ketones and five acyclic aldehydes toward the electron donors, diethylamine (DEA) and triethylamine (TEA), by monitoring amine quenching of carbonyl fluorescence. Observed bimolecular rate constants for quenching,  $k_q$ , are obtained from Stern-Volmer treatments of fluorescence quenching as a function of amine concentrations and the measured carbonyl fluorescence lifetime,  $\tau_f$ . The effects of carbonyl and amine structure, as well as the nature of the solvent, on the observed  $k_q$  values are determined. We will note several key observations. (1) The  $k_q$  values for the ketones are found to be very sensitive to  $\alpha$ -methyl substitution. For example,  $k_q$  for TEA quenching of acetone  $^1n, \pi^*$  states is  $2.7 \times 10^9 M^{-1} s^{-1}$ , while  $k_q$  for TEA quenching of  $^1n, \pi^*$  states of di-*tert*-butyl ketone is  $< 4 \times 10^6 M^{-1} s^{-1}$ . (2) DEA, although it has a higher oxidation (or ionization) potential than TEA, is consistently a somewhat better quencher of carbonyl excited singlets in hexane than TEA. (3) The observed  $k_q$  values are only minimally effected by solvent changes. (4) Acetone  $^1n, \pi^*$  states are determined to be about an order of magnitude more reactive toward amine quenching than acetone  $^3n, \pi^*$  states. (5) Alkanal  $^1n, \pi^*$  states are found to be 5 - 10 times more reactive toward TEA quenching than alkanones  $^1n, \pi^*$  states.