$$CH_3\diagdown C \diagup N \atop Cl \diagup ~ \diagdown N \qquad \xrightarrow{h\nu}$$

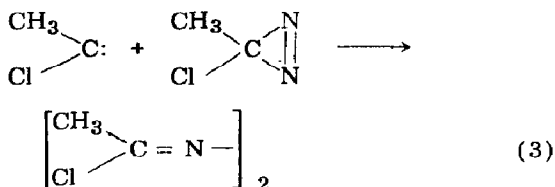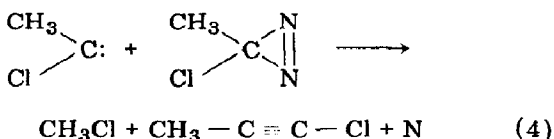$$CH_2 = CHCl + HC \equiv CH + HCl + N_2 \quad (2)$$

Initial results suggest that the mechanism for the photochemical reaction is similar to that proposed by Frey and Stevens for methyldiazirine [5]. That is, two unimolecular channels are available from the excited state: a low energy triplet path leading to the products of reaction (1); and a singlet path with sufficient energy to form the fragmentation products.

Preliminary results suggest that bimolecular collisions between methyl chloro-carbene and the ground state of I may lead to reaction. Two reaction paths are possible. The first leads to an azine. Azines are well-known decomposition products of diazirines [6].

$$CH_3\diagdown C: ~+~ CH_3\diagdown C\diagup N \atop Cl \diagup \qquad Cl \diagup ~ \diagdown N \qquad \longrightarrow$$

$$\left[ CH_3\diagdown C = N - \atop Cl \diagup \right]_2 \qquad (3)$$

The second path involves elimination of nitrogen.

$$CH_3\diagdown C: ~+~ CH_3\diagdown C\diagup N \atop Cl \diagup \qquad Cl \diagup ~ \diagdown N \qquad \longrightarrow$$

$$CH_3Cl + CH_3 - C \equiv C - Cl + N \qquad (4)$$

The fragmentation products of the photochemical reaction (2) have attracted our interest. Since the activation energy for elimination of hydrogen chloride from ground-state vinyl chloride is too high [7] to reasonably account for the yield of acetylene and hydrogen chloride, an electronically excited state of vinyl chloride is likely involved. It is well known that photolysis of vinyl chloride effects elimination of hydrogen chloride [8] which, under conditions of flash photolysis, has a sufficiently inverted vibrational population to support laser action [9].

These considerations together with the analogy of eliminations from ion-radicals analogous to methylcarbenes [10] suggest that the hydrogen chloride produced in photolysis of I may have a significant inversion of vibrational population. Intensive efforts are under way to demonstrate this by detecting a laser pulse after flash photolysis of I.

1  M. T. H. Liu and D. H. T. Chien, J. C. S. Perkins II, (1974) 973.
2  M. R. Bridge, H. M. Frey and M. T. H. Liu, J. Chem. Soc. (A), 91 (1969)
3  R. A. Moss and A. Mamantov, J. Amer. Chem. Soc., 92 (1970) 6951.
4  M. T. H. Liu, unpublished results.
5  H. M. Frey and J. D. R. Stevens, J. Chem. Soc., (1965) 1700.
6  A. Padwa and D. Eastman, J. Org. Chem., 34 (1969) 2728.
7  P. Cadman and W. J. Engelbrecht, Chem. Comm., (1970) 453.
8  P. Ausloos, R. E. Rebbert and M. H. J. Wijnen, J. Res. Nat. Bur. Stand. (U.S.), 77A (1973) 243.
9  M. J. Berry, J. Chem. Phys., 61 (1974) 3114.
10 D. H. Williams and G. Hvistendahl, J. Amer. Chem. Soc., 96 (1974) 6753 and 6755.

γ6
## Quenching of the Norrish Type II Reaction of Butyrophenone by Thiophenic Compounds

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In order to better understand the nature and energy content of the excited states of five membered heterocyclic compounds a study of quenching of the triplet state of butyrophenone by thiophenic compounds was carried out. The studies were performed in cyclohexane solutions, at 25 °C. The following quenching rate constants were determined from the Stern Volmer plots for reaction (5).

$$^3Bu + TH \xrightarrow{k_5} \text{quenching} \qquad (5)$$
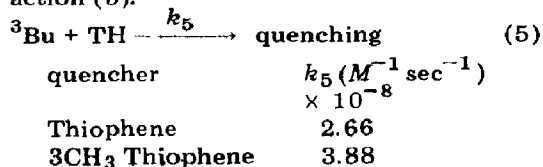
| quencher | $k_5 (M^{-1} sec^{-1})$ $\times 10^{-8}$ |
|---|---|
| Thiophene | 2.66 |
| 3CH$_3$ Thiophene | 3.88 |

| | |
|---|---|
| 2 Cl Thiophene | 6.65 |
| 2CH$_3$ Thiophene | 17.32 |

These data correlate well with the ionization potentials calculated for the quenchers from charge transfer complexes studies previously done, and therefore a mechanism involving a charge transfer complex formed between the excited butyrophenone in its triplet state and the quencher is postulated. According to the mechanism the energy content of the triplet states of the thiophenic compounds used in this work should be greater than 74.1 kcal/mole which is the energy content of the $^3$Bu.

## δ3
## Photoionization Processes at Threshold: Direct and Auto-Ionization and Franck-Condon Factors for Simple Molecules

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A threshold photoelectron-coincident photoion spectrometer has been constructed using a collimated hole structure for selection of near-thermal electrons. Calibration with rare gases demonstrated a resolution of 0.014 ev FWHM. Location of maxima is possible within less than 0.005 ev. Threshold photoelectron spectra lead directly to transition probabilities at threshold for direct processes, without concern for variation in the ionization cross section past onset. Contributions from intense autoionizing states just above the onset of direct processes introduce a complication resulting from incomplete rejection. Preionization can be identified by relative abundance measurements of threshold photoelectrons and photoions, or by reducing the resolution of the threshold detector by increasing the extraction field in the ionization region. Vibrational structure between the first and second electronic states of the ions is difficult to assess quantitatively because of such interferences; these become less important for higher electronic states. Comparison of our results with data obtained by other methods is made for the rare gases, nitrogen and carbon dioxide, and measurements on BF$_3$, SF$_6$, and other small inorganic fluorides will be summarized.

## δ4
## Photoionization Mass Spectrometry of Alcohols, Alcohol Clusters and Carbon Dioxide Dimers

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Photoionization of hydrogen bonded alcohol clusters and clusters of carbon dioxide has been studied using a supersonic molecular beam sampling system, wavelength dispersed vacuum ultraviolet radiation produced from an electron storage ring, and a quadrupole mass spectrometer ion detector. In addition to a regular spectrum, the observed $m/e$ intensities for methanol and ethanol samples display ions corresponding to the series $(ROH)_nH^+$, where $1 \leqslant n \leqslant 5$. From mixtures of methanol and ethanol, a complete series of mixed clusters $H^+(CH_3OH)_n(CH_3CH_2OH)_{4-n}$ $0 \leqslant n \leqslant 4$, was observed. Experiments performed to elucidate how and where these clusters are formed indicate that neutral cluster species are present in the sample gas in the molecular beam source chamber at pressures above 10 Torr, and that equilibrium conditions may exist above 35 Torr at 20 °C. Photoionization efficiency curves for the methanol cluster species show appearance potentials in the order $m/e$ 129(9.3 eV) < 97(9.5 eV) < 65(9.8 eV) < 33(10.2 eV) < 32(10.84 eV). This ordering, as well as high observed cluster ion intensities and low equivalent pressures in the ion source, leads us to exclude ion—molecule reactions as the major source of the detected ions.

If an equilibrium process is assumed for the neutral cluster and each cluster produces a unique ion, the relative intensities of the cluster ions as a function of molecular beam source gas temperature can produce thermochemical information on the following neutral cluster equilibria:

$$(CH_3OH)_n \rightleftharpoons (CH_3OH)_{n-1} + CH_3OH \quad (1)$$
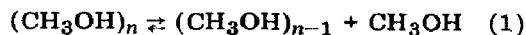
where the cluster association is assumed to arise from hydrogen bonding. Linear van 't Hoff type plots are obtained for