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K5

LIPS Studies of Primary Processes in The Photodissociation of C_2N_2 and C_4N_2

M. J. SABETY-DZVONIK, R. J. CODY and W. M. JACKSON*

*Astrochemistry Brand, Goddard Space Flight Center NASA, Greenbelt, Md. 20770 (U.S.A.) and *Howard University Department of Chemistry, Washington, D.C. 20059 (U.S.A.)*

The advent of tunable dye lasers has revived interest in the use of photoluminescence spectroscopy as a technique for characterizing the transient intermediates that occur in chemical processes. The spectral brightness of these lasers allows the selective excitation of free radicals such as CN, C_2 , OH, etc., to an excited electron level from an individual quantum level in the lower state. The photons that result from the radiative decay of this excited state can be used to measure the number of free radicals originally present in the lower state. This technique called laser-induced photoluminescence spectroscopy (LIPS) has been used to study the primary photodissociation processes in C_2N_2 and C_4N_2 .

The photon energy of the dissociation vacuum ultraviolet radiation was limited by a sapphire window to wavelengths greater than 1450 Å. Time dependent LIPS studies of the CN fragment produced from the photolysis of C_2N_2 have shown that roughly equal amounts of X state and A state radicals are produced in this wavelength region, which suggest that this is the principal primary process in the dissociation of C_2N_2 . Similar studies have also been done for C_4N_2 and will be reported on.

A holographic grating monochromator has been used to discriminate between fluorescent radiation from the excited radical and scattered flash lamp light. This has permitted us to make LIPS measurements within 3 μ s of the flash at a total of C_2N_2 or C_4N_2 pressure of 10 μ m. These studies have shown conclusively

that the X state radical is produced in high rotational levels as a result of the dissociation of either compound. The surprising thing about the observed rotational distributions is that they are Maxwellian with a rotational "temperature" of 1500 and 1400 K for C_2N_2 and C_4N_2 respectively. These observations can be explained in terms of a simple impulse model for photodissociation.

In both C_4N_2 and C_2N_2 most of the X state radicals are formed in the $v'' = 0$ level. A considerable fraction of the observed radicals, 30% for C_2N_2 and 15%, do, however, appear in the $v'' = 1$ level of the X state. These observations suggest that the C-N internuclear distance in the excited states of C_4N_2 and C_2N_2 responsible for the photodissociation is near the r_{CN} distance in the X state of CN.

K6

Collision-Induced Electronic Relaxation in Polyatomic Vapors

A. E. W. KNIGHT and C. PARMENTER
Chemistry Department, Indiana University, Bloomington, Ind., (U.S.A.)

Work in various laboratories has shown that the vapor fluorescence of a number of molecules is quenched by added gases. Every adduct so far tried is effective in quenching and the cross sections are often on the order of hard sphere. The quenching generally follows Stern-Volmer kinetics (not necessarily simple Stern-Volmer kinetics) and the fluorescence decay is found to be exponential.

These observations apply to formaldehyde [1], glyoxal [2, 3], propynal [4] and pyrimidine [5]. With the exception of formaldehyde, at least a significant component of the collision-induced S_1 decay is known to be triplet formation. The evidence in glyoxal is most compelling since the growth of triplet population accompanying singlet decay can be monitored directly by phosphorescence [3]. Sensitized biacetyl phosphorescence has been used to establish that collisions control the $S_1 \rightarrow T$ intersystem crossing in pyrimidine [5].

Cross sections for collision-induced triplet formation in pyrimidine, propynal and glyoxal seem not to be influenced by special heavy atom effects or oxygen

effects which may modify the $S_1 - T$ electronic matrix elements. A good correlation between the cross sections and intermolecular potential well depths has been found [5].

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K7

The Photodissociation, with Pulsed Synchrotron Radiation, of H_2 and D_2 near 750 Å

P. BORRELL

Department of Chemistry, University of Keele, Staffordshire (U.K.)

P. M. GUYON

Laboratoire de Photophysique Moléculaire, Orsay (France)

M. GLASS-MAUJEAN

Laboratoire de Spectroscopie Herzienne de l'Ens Paris (France)

Emission of the Balmer α , β and γ lines of atomic H and D were observed when H_2 and D_2 were irradiated below 750 Å with synchrotron radiation from the ACO storage ring at Orsay. The excitation spectra were recorded together with that from the Lyman α emission below 850 Å and the lifetime of the β emission was measured by single photon counting.

The excitation spectra were structured and some of the peaks could be correlated

with the absorption spectrum in this region. The spectra indicate that the atoms are formed principally by predissociation from the initially excited Rydberg states in the region just above each energy threshold.

L7

Photochemistry of Ru(II) Complexes in Non-Aqueous Solvents

G. B. PORTER and P. E. HOGGARD

Department of Chemistry, University of British Columbia, Vancouver, B.C. V6T 1W5 (Canada)

Tris(bipyridyl)ruthenium(II) is now frequently used as a sensitizer for transition metal complexes, both for luminescence and for photochemistry. However, in solvents less polar than water, it does undergo a photochemical reaction itself. Although this reaction has only a small quantum yield (10^{-3}), it must still be taken into account in sensitization studies because the ruthenium complex has a very high extinction coefficient in the visible region and it is therefore used in quite low concentrations.

The reaction of the NCS^- salt in DMF leads to two products, one of which is the $cis(Ru(bipy)_2(NCS)_2)$, and the other is the $cis(Ru(bipy)_2(NCS)(DMF))^+$. The former is formed from an ion paired excited state with a quantum yield:

$$\Phi = \Phi_{ip} \frac{K_{ip}(NCS^-)}{1 + K_{ip}(NCS^-)}$$

with $\Phi_{ip} = 1.4 \times 10^{-3}$ and $K_{ip} = 55 \pm 10$.

The second species is formed with a quantum yield of ca. 3.2×10^{-4} , independent of (NCS^-) . The photochemical reaction is quenched by O_2 to the same extent as is phosphorescence, thus the phosphorescing triplet state is also directly involved in the photoreactions.

O2

Intramolecular Excimers

W. KÜHNLE and K. ZACHARIASSE

Max-Planck-Institut für biophysikalische Chemie, Göttingen (Germany)

Formation of intramolecular excimers with molecules $A-(CH_2)_n-A$ has in general been observed only for $n = 3$, e.g. for 1,3-diphenylpropane but not for 1,4-diphenylbutane (Hirayama [1]). The only