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Authors

Chesko, J.D.
Suits, Arthur G.
Lee, Yuan T.

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J.D. Chesko, A.G. Suits, and Y.T. Lee

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Pyrazine: Supercollisions or Simple Reactions?

James D. Chesko, Arthur G. Suits, and Yuan T. Lee

Department of Chemistry
University of California, Berkeley

and

Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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James D. Chesko, Arthur G. Suits and Yuan T. Lee

*Dept. of Chemistry, University of California at Berkeley and
Chemical Sciences Division, Lawrence Berkeley Laboratory
Berkeley, California 94720*

Abstract:

Photodissociation of 1,4 Diazine (Pyrazine) following 248nm ($S_2 \leftarrow S_0$) and 308 nm ($S_1 \leftarrow S_0$) excitation has been studied by photofragment translational spectroscopy.

While the latter wavelength was inefficient at generating reactive products, the former wavelength afforded a rich variety of fragments, the most translationally energetic being HCN carrying up to 36 kcal/mol. The implications of this reactive mechanism towards interpretation of vibrational energy transfer experiments from hot ground state pyrazine are considered. The absolute quantum yields $\phi(248\text{nm}, 27\text{-A}) = 0.40 \pm .10$, $\phi(248\text{nm}, 27\text{-B}) = 0.08 \pm .02$, $\phi(308\text{nm}, 27\text{-B}') = 0.003 \pm .001$ and the two corresponding translational energy distributions are presented.

Communication:

Describing intermolecular vibrational relaxation rates in relation to competing processes directing energy flow is fundamental to understanding chemical reactivity. Modern studies have progressed in detail far beyond determination of the pressure and temperature dependence of reaction rate coefficients.¹ The spectroscopic properties of

pyrazine, namely its propensity both to fluoresce and phosphoresce, have made it a model system to study vibrational energy transfer following photo-excitation. Single vibronic level decay can be measured by monitoring fluorescence from the first excited singlet state² or phosphorescence from the first triplet state.³ Studies attempting to extend the range of available energy are challenged by the sharp drop off in fluorescence yield from the higher excited states and fast radiationless processes which occur.⁴ An ingenious method which recaptures the level of quantum state detail is to monitor the relaxation processes via interrogation of the bath molecules which accept energy from the more complex donor molecules.⁵ When the electronic relaxation mechanisms are well known,⁶ one can describe the energetically activated donor with confidence, and focus experimental efforts on characterizing changes in the acceptor, allowing characterization of rotational, translational and vibrational energy transfer to the simpler bath molecules after single collision excitation.^{5b} The energy transfer characteristics can then be modeled and described within the framework of collision geometries,² angular momentum constraints⁷ and vibrational degrees of freedom.⁸

As detailed and sensitive as the measurements of the bath molecules may be, they are also blind to the identity of the perturbation they seek to characterize. The influence of a 'reactive component' inducing the bath excitation has been an obvious concern that is handled as carefully as possible in such studies.⁹ Mullin et al.^{5b} report high rotational and translational excitation following collision of excited pyrazine with CO₂. It is surprising that a large fraction of internal energy from a rather complex polyatomic molecule could be transferred to a triatomic as seen in these studies. The object of this

communication is to report the observation of fast HCN produced in the UV photodissociation of pyrazine and consider its possible influence on energy transfer studies.

The azabenzenes, or nitrogen substituted benzene compounds, are known to liberate translationally fast HCN following photoexcitation.¹⁰ Previous photochemistry studies of the diazines have focussed primarily upon isomerization processes.¹¹ Using the method of photofragment translational spectroscopy delineated earlier¹² we found a rich variety of products that soon will be described in detail.

The apparatus, which has been described elsewhere,¹² features a pulsed molecular beam of pyrazine seeded in helium carrier gas, which is crossed at 90 degrees by the output of an excimer laser under collision-free conditions. Photofragments scatter into a triply differentially pumped UHV detector consisting of an electron bombardment ionizer, quadrupole mass filter and Daly ion counter, where they are counted as a function of flight time, scattering angle and product mass. Time-of-flight spectra for $m/e=27$ and its momentum matched $m/e=53$ partner are shown in figure 1. The translational energy distributions obtained by forward convolution fitting these time-of-flight spectra are shown in figure 2. Three contributions are seen, labeled 27-A for the fastest component, 27-B for the second component and 27-C for the slowest component; their origin has been discussed¹³ and will be presented in a future publication. The quantum yields $\phi(248\text{nm},27\text{-A})=0.40$, $\phi(248\text{nm},27\text{-B})=0.08$ were estimated from absolute photodissociation cross section measurements determined by a hole-burning experiment we performed combined with published absorption cross section

measurements.¹⁴ At the longer wavelength $\phi(308\text{nm}, 27\text{-B}) = 0.003$, although this value could be inaccurate due to narrowing in the jet absorption line. The implications for energy transfer studies in particular arise from the significant high energy component of channel 27-A. We estimate the quantum yield for production of HCN with greater than 1 eV translational energy to be 14%. Concentrating upon this fast tail of the first channel we consider the energetic limits of HCN/CO₂ collisions.

The collision between two closed-shell, relatively 'stiff' species with a mass ratio of 5:8 allows for very efficient translational ($T \rightarrow T$) and rotational ($T \rightarrow R$) energy transfer as well as possible vibrational excitation. For a 'head-on' collision between HCN and CO₂ 1.0 eV of translational energy may be transferred; Mullin et al^{5b} measure translational energy changes up to 0.7 eV (relative velocity corrected). We can estimate the amount of rotational excitation possible using a simple impulsive model¹⁵ as up to 1/3 of the excess (translational energy), or up to 0.5 eV; Mullin et al^{5b} measure up to 0.3 eV ($J=82$). The 'breathing ellipsoid' model of Flynn¹⁶ predicts that geometries slightly displaced from a direct end-on collision will contribute most to rotational excitation. The efficiency of energy transfer from HCN to CO₂ by such a mechanism will be significant by virtue of the like masses of each particle. Time dependent properties of a kinetic model due to collisions and diffusion will be similar for any collision partner (excited pyrazine, HCN) formed from photoexcitation. The kinetic rate constants k^J/Z which fall into the range 1/30 to 1/100^{5b} per collision match reasonably the estimated quantum yields. The HCN photoproducts were ultimately detected at intensities of 0.2 MW/cm² (3 mJ/cm² excimer pulse) at 248 nm and 3 MW/cm² at 308

nm with a linear power dependence, roughly the field strengths associated with an unfocused excimer beam.

The implications of these results of vibrational energy transfer are less clear. Broadside collisions can excite the ν_2 bend while end-on impacts are expected to cause a slight amount of ν_3 (asymmetric stretch) motion with less concomitant rotational excitation. The 2349 cm^{-1} (0.3 eV) required for one quanta of ν_3 excitation is energetically possible. Another excitation mechanism could involve vibrational to vibrational (V $\rightarrow$ V) energy transfer from vibrationally excited HCN liberated in the photodissociation process. The vibrational frequencies of HCN, notably 2096 and 3312 cm^{-1} , are reasonably well matched to the CO_2 species.

A more direct method of evaluating the role of HCN would be to attempt to measure its translational, vibrational and rotational energy directly. Based upon the wavelength dependent quantum yields one would also predict large energy transfer following 308 nm excitation to be drastically lower than 248 nm, while if collisions with hot ground state pyrazine dominate the 20% reduction in internal energy should have a more modest effect. Photodissociation of 'donors' such as tetrazine and triazine are expected to show similar excitation characteristics to the HCN produced from pyrazine.

The photoreactive behavior of pyrazine at 248 and 308 nm exhibits a dramatic change which may have importance in the interpretation of collisional relaxation studies. The quantum yields, translational energy release and expected collisional behavior of the energetic HCN photoproducts suggest a different explanation¹³ for the phenomenon of 'supercollisions' involving pyrazine.

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Figure Captions

Figure 1. Time-of-flight spectra of HCN ($m/e=27$) taken at 30 degrees and its momentum matched partner, C_3H_3N ($m/e=53$), taken at 15 degrees relative to the molecular beam in the laboratory frame following 248 nm excitation. The two peaks with the shortest arrival times represent channels 27-A and 27-B, respectively. The slowest peak is from an additional HCN photodissociation channel, channel 27-C.

Figure 2. The probability of translational energy release used to fit the two fastest components (channels 27-A and 27-B) of the HCN/ C_3H_3N time-of-flight. For channel 27-A, the maximum energy released is 54 kcal/mol, while on average about 25 kcal/mol is partitioned into translational motion upon photodissociation. For channel 27-B, the maximum translation energy liberated is 16 kcal/mol, with an average of about 8 kcal/mol.

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Translational Energy (kcal/mol)

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720