

KINETIC SPECTROSCOPY USING A COLOR CENTER LASER

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The powerful method of infrared kinetic spectroscopy¹ has been applied to the investigation of the reaction between NH_2 and NO . The amidogen radical, NH_2 , was produced in high concentrations by photolysis of NH_3 with the 193 nm ArF line of an excimer laser. Probing with a high resolution color center laser spectrometer combined with fast infrared detectors allowed the NH_3 , H_2O , NO and NH_2 and OH radicals to be monitored on microsecond time scales.

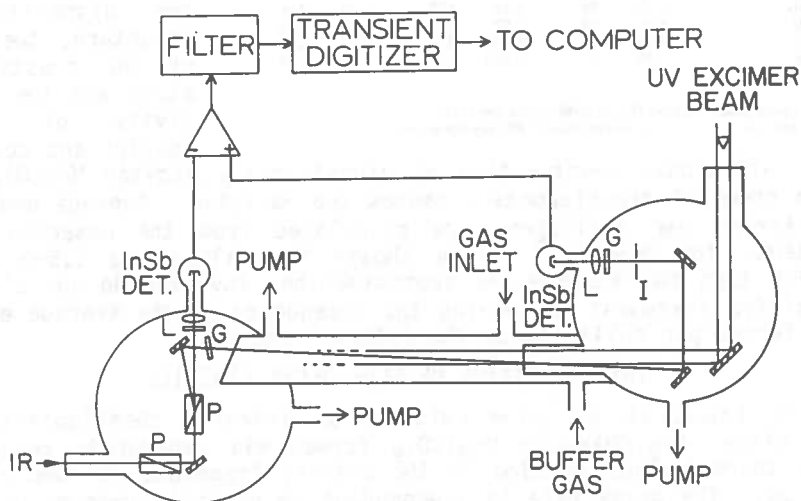
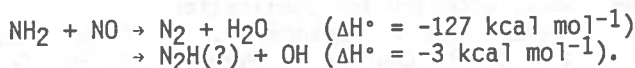


Fig. 1. Experimental layout. P = polarizer, G = germanium flat, L = lens, I = iris.

The $\text{NH}_2 + \text{NO}$ reaction, proposed as a key step in the industrially important "Thermal DeNOX" process, has been studied extensively by others. The rate constant ($\sim 1.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) has been measured by several workers²⁻⁴ and the two major product channels are generally agreed to be



Determination of the branching ratios of these two channels, however, has been somewhat more elusive.

INTERPRETATION OF FAST DECAY KINETICS

A linear pressure dependence is observed for the pseudo-first-order decay rates of the fast component for seven buffer gases indicating that vibrationally excited $\text{Mn}(\text{CO})_5$ decays by collisional deactivation. Table II compares the second order rate constants for collisional deactivation of $\text{Mn}(\text{CO})_5$ with published data obtained

TABLE II. Phenomenological Second-Order Rate Constants* and Average Energy Transferred per Collision^b for Vibrational Collisional Deactivation

Collider Gas	$\text{Mn}(\text{CO})_5$		Azulene			
	(15 kcal mol ⁻¹) ^c 10 ¹¹ k	(ΔE)	(48 kcal mol ⁻¹) ^c 10 ¹¹ k	(ΔE)	(85 kcal mol ⁻¹) ^c 10 ¹¹ k	(ΔE)
$\text{Mn}_2(\text{CO})_{10}$	27.4	325	—	—	—	—
Azulene	—	—	25.2	1217	13.6	1425
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	9.26	216	11.7	707	9.41	1234
NO	4.99	110	—	—	—	—
CH_4	4.92	78	3.10	173	3.70	448
CO	3.75	77	1.92	151	2.20	375
Ar	3.24	80	1.29	119	1.07	215
He	1.69	17	0.663	37	0.69	83

* From linear least-squares fits of data; units are cm³s⁻¹.

^b Units are cm⁻¹. ^c average excess vibrational energy

with the same technique for highly vibrationally excited azulene.⁵ The deactivation rates for $\text{Mn}(\text{CO})_5$ and azulene are remarkably similar given the disparity in structure, the mass of the constituent atoms and the reactivity of these species and confirm that collisional deactivation of vibrationally excited $\text{Mn}(\text{CO})_5$ and not a chemical transformation causes the emission. Average energies transferred per collision were calculated from the observed rate constants for $\text{Mn}(\text{CO})_5$.⁵ Even though the values are 1.5-3 times smaller than for azulene the approximations involved do not allow a definitive statement concerning the dependence of the average energy transferred per collision on the internal energy.

INTERPRETATION OF SLOW DECAY KINETICS

We interpret the slow emission as infrared chemiluminescence from either $\text{Mn}_2(\text{CO})_{10}$ or $\text{Mn}_2(\text{CO})_9$ formed via exothermic reactions since thermal equilibration of the primary fragments is complete in $\ll 1$ ms. The decay rate is independent of partial pressure of non-reactive buffer gases so diffusion of emitting species from the detection volume cannot account for the observed decay. Similarly thermal conduction effects are negligible since the calculated temperature jump ($<20^\circ\text{K}$) is insufficient to observe infrared emission. We are continuing to investigate the chemistry leading to the slow decay.

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The current work indicates that the OH channel accounts for $13 \pm 2\%$ of the reaction. Measurements of OH lines were made with and without NO_2 added to the reaction mixture. The reaction of NO_2 with the H atoms formed in the NH_3 photolysis forms OH radical, and thus gives a measure of NH_2 produced. Comparison of the OH signal with and without NO_2 enables the calculation of the percentage of NH_2 which reacts to form OH.

Two different pairs of NH_3 and H_2O lines were measured with 20 Torr of buffer gas to minimize the temperature rise of the system. Values of 0.85 ± 0.09 and 0.66 ± 0.03 for the ratio of H_2O formed to NH_3 photolyzed come close to representing a "materials balance" with the contribution of the OH channel. All of the H_2O signals exhibited a pronounced induction period suggesting that H_2O is formed in high vibrational states. The behavior of the signals were consistent with simulations in which a stepwise sequential loss of vibrational energy occurs with equal quenching cross-sections for each step.

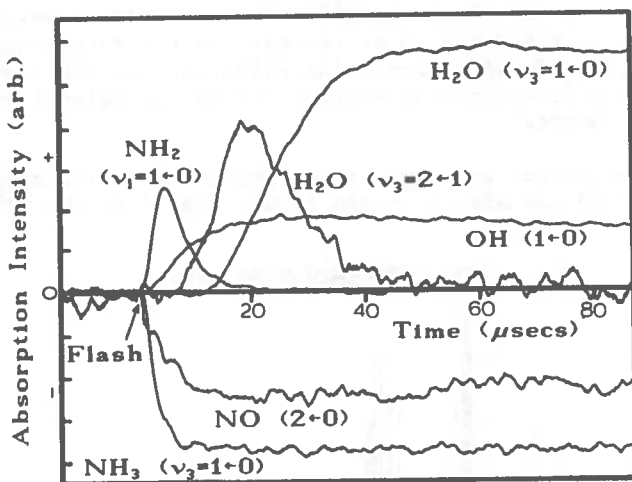


Fig. 2. The time behavior of a variety of species can be monitored. (Initial conditions, $P_{\text{NH}_3} = 70$ mTorr, $P_{\text{NO}} = 1$ Torr, and $P_{\text{He}} = 8$ Torr.)

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