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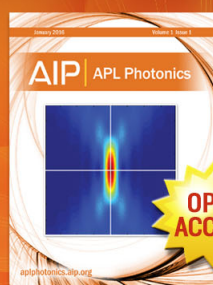J. Chem. Phys. **106**, 3876 (1997); 10.1063/1.473109

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The unimolecular reaction of $(CH_3)_3CNO$ following n–π* excitation with a tunable dye laser[a]

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The predissociation of $(CH_3)_3CNO$ following the 570–710 nm laser excitation of the n-π* transition is reported. The small fluorescence quantum yield and its short lifetime (< 20 ns) indicate efficient radiationless processes prior to dissociation. NO is the major dissociation product and its concentration was monitored in real time by using the two-photon laser excited fluorescence technique. The NO yield as a function of wavelength followed very closely the absorption contours of $(CH_3)_3CNO$. The NO production rate was $> 10^8$ s^{-1} at all wavelengths studied and this rate is too fast to be consistent with a mechanism involving a radiationless transition to the ground electronic state followed by energy randomization and dissociation. Alternative predissociation mechanisms are considered.

I. INTRODUCTION

Recently, there has been considerable interest in state-to-state unimolecular reactions of polyatomic molecules. In an ideal experiment, one would like to excite a molecule to a single level above the dissociation threshold, and then monitor its dissociation in real time and determine nascent quantum state distributions among the reaction products. Real time measurements of unimolecular reaction rates may serve to test theories of unimolecular decay (e.g., RRKM), whereas nascent state distributions among reaction products should prove enlightening with respect to the dynamics of the photodissociation event. Unimolecular reactions of small molecules often proceed very rapidly, and cannot be observed using conventional techniques with temporal resolution >1 ns. Thus, excitation of medium or large molecules to near threshold energies is desired. Exciting overtone vibrations of molecules can provide direct access to vibrational levels of the ground electronic state that are above the dissociation threshold.[1,2] However, due to the very small cross section for high overtone absorption, signals are very small, and the technique is most suited to molecules with high frequency vibrations and low dissociation energies. A way to circumvent the low absorption cross sections is to excite an electronic state of the molecule, which predissociates following fast internal conversion and/or isomerization to the ground electronic state manifold.[3-5] Alkyl nitroso compounds (R–NO) seem to be good candidates for such studies. They exhibit absorption features in the 500–750 nm wavelength region that are assigned to an n-π* transition,[5,6] whose origin lies close to the threshold for dissociation to ground state R + NO. They also undergo efficient dissociation upon excitation at these wavelengths.[5]

The predissociation of CF_3NO has recently been stud-

ied in some detail.[7,8] Fluorescence lifetime measurements of laser excited CF_3NO have shown that the observed lifetimes following n-π* excitation are much shorter than those anticipated from the integrated absorption coefficient, and indicate the existence of a fast radiationless process which competes with radiative decay.[8] In their study of CF_3NO dissociation dynamics, Roellig et al. found that the appearance time of NO is similar to the fluorescence lifetime of laser excited CF_3NO, and concluded that the unimolecular reaction rate of the excited CF_3NO is controlled by the rate of the radiationless process followed by very rapid dissociation.[7(b)] They suggested that the dissociation involves the ground state (S_0), and/or the lowest triplet state (T_1) as intermediates. Spears and Hoffland used fluorescence lifetime measurements and collisional quenching studies to support a model involving internal conversion (IC) of the excited state (S_1) to S_0 followed by rapid dissociation to $CF_3 + NO$.[8(b)] Since the measured IC rates are apparently slower than the unimolecular reaction rates, it is impossible to estimate the dissociation rate of CF_3NO from S_0 of T_1. Very recently, the dissociation of NCNO to CN and NO was studied following n-π* excitation at 532 nm.[9] Again, dissociation following fast IC to S_0 was proposed, but no rates could be measured.

Our aim in this study was to find an alkyl nitroso compound which is structurally and spectroscopically similar to CF_3NO, but which has a large number of vibrational degrees of freedom. We anticipated that the unimolecular dissociation rate would then be slower than the radiationless transition rate, and thus directly measurable from the appearance of NO. $(CH_3)_3CNO$ (2-methyl-2-nitroso propane, hereafter referred to as t-BuNO) was chosen since its absorption spectrum in the 530–740 nm region is very similar to that of CF_3NO, and is assigned to the n-π* transition,[5] and its dissociation energy is comparable to that of CF_3NO.[10] However, it has 39 vibrational degrees of freeom as compared with 12 for CF_3NO. The thermal unimolecular reaction of t-BuNO was studied by Choo et al.[10] who reported a frequency factor $A_\infty = 10^{15.6\pm0.5}$ s^{-1}, an activation energy $E_{a\infty} = 36 \pm 1$ kcal mol^{-1} (where the ∞ sign stands for high pressure parameters), and a C–NO bond dissociation
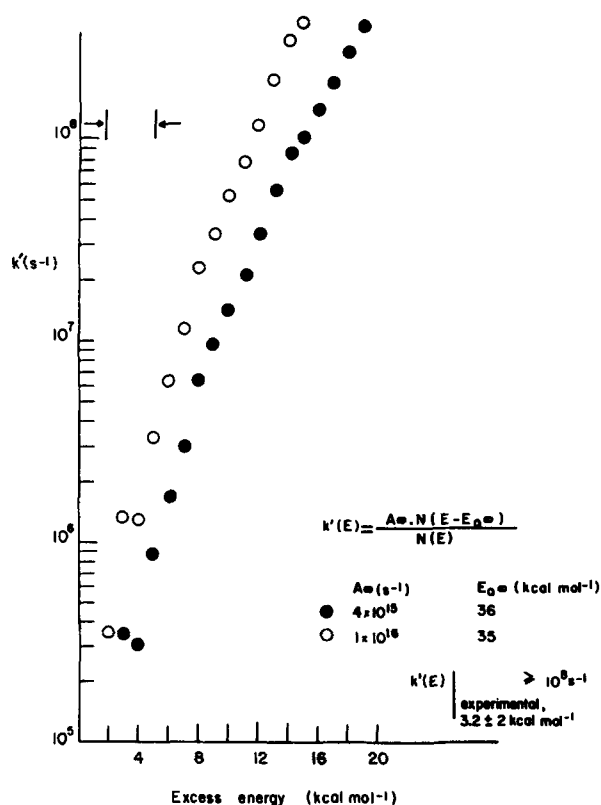
FIG. 1. Energy dependence of $k'(E)$ (energy E in excess of the threshold energy) calculated from Eq. (1) using experimental A_∞ and $E_{a\infty}$ of Ref. 10, and the t-BuNO vibrational frequencies: 2990(6), 2890(3), 1585(2), 1570, 1485(4), 1370(3), 1250, 1220(2), 1030(2), 940(3), 810, 760, 650, 450, 441, 400(2), 300(2), 280(2), 220. ● - $A_\infty = 4 \times 10^{15}$ s^{-1}; $E_{a\infty} = 36$ kcal mol^{-1} (average values from Ref. 10); O- $A_\infty = 1.0 \times 10^{16}$ s^{-1}; $E_{a\infty} = 35$ kcal mol^{-1} [upper limit for $k'(E)$ from data of Ref. 10]. The densities of states, $N(E)$, were calculated using the Whitten–Rabinovitch approximation. $N(E - E_{a\infty})$ was calculated using direct counting of vibrational states with frequency grouping (see Sec. IV for details). The irregular behavior of $k'(E)$ vs E near threshold is a result of using the direct counting routine. The two vertical lines at the upper left side indicate the upper limit of the measured appearance rate of NO, and our estimate of the excess energies achieved by excitation of 710 nm (see the text).

energy of 39.5 ± 1.5 kcal mol^{-1}.

According to Forst,[11,12] the unimolecular reaction rate at energy E, $k'(E)$, can be deconvoluted from the thermal average using the equation

$$k'(E) = \frac{A_\infty N(E - E_{a\infty})}{N(E)}, \quad E > E_{a\infty}, \quad (1)$$

where $k'(E) = f_\infty k(E)$ is the dissociation rate including centrifugal effects and is averaged over the angular momenta of the reactants (f_∞ is the high pressure centrifugal correction factor[11,12]). $N(E)$ is the density of states of the molecule at energy E, and $N(E - E_{a\infty})$ is its density of states at an excess energy $E - E_{a\infty}$ above dissociation threshold. The results of such a deconvolution using the thermal data for t-BuNO are shown in Fig. 1. They demonstrate that at excess energies of 3 to 10 kcal mol^{-1} (achieved via laser excitation in the region

600–710 nm of room temperature t-BuNO) lifetimes of 3300 to 70 ns, respectively, are to be expected (see Sec. IV). Such lifetimes should be easily measured using our experimental arrangement. Our results show however, that NO appearance times at these excess energies are shorter than 10 ns, and therefore they cannot be explained by a statistical unimolecular reaction on the ground electronic state potential surface.

II. EXPERIMENTAL

The experimental apparatus was similar to that used by Roellig et al.[7(b)] and will therefore be described only briefly. The fluorescence chamber was made of Al and fitted with quartz windows. The photolyzing laser was a Nd:YAG laser pumped dye laser (Quanta Ray), and wavelengths in the range of 570–750 nm were achieved using the dyes rhodamine 590 and 640, and LDS 698 and 750. Typical pulse energies were 5–20 mJ at 6 ns FWHM. The laser output was brought to a focus at the center of the chamber using 15–100 cm focal length (f. l.) lenses. NO was monitored using the two photon laser excited fluorescence (TPEF) technique.[7] The counter-propagating probe laser beam was generated by a N_2 laser pumped dye laser (Molectron DL-II) using coumarin 460 dye, and brought to a focus at the center of the chamber with a 15 cm f. l. lens. Timing between the lasers was controlled as follows: The Nd:YAG laser flashlamps and Q-switch were triggered externally, and the delay between them was optimized for maximum output. The delay between the Q-switch triggering pulse of the Nd:YAG laser and the N_2 laser triggering pulse was determined by a delay generator with 10 ns resolution (BNC 7055), thus accurately controlling the delay between the photolysis and probe laser pulses (jitter ± 5 ns). TPEF was observed perpendicularly to the laser beams' direction using a solar blind photomultiplier (PMT, Hamamatsu HU166), and scattered light was eliminated by the use of one or two Corning 7-54 glass filters. Laser excited fluorescence of t-BuNO following $n-\pi^*$ excitation was detected with a cooled PMT (RCA 31034). Scattered laser light was eliminated by using long baffle arms at the entrance and exit of the laser beam, and cutoff filters (Corning 7-59 or 5-57) in front of the PMT. The output from the PMT was processed either with a boxcar integrator (PAR 162/165), or a digital oscilloscope (Nicolet, Explorer III) interfaced to a small laboratory computer (HP 9835A).

t-BuNO was obtained as a stable dimer (Aldrich). The monomer was generated by mild heating at 80 °C, and stored in the dark. Fresh samples were prepared immediately prior to an experiment.

III. RESULTS

A. Laser fluorescence excitation of t-BuNO

A portion of the low resolution, room temperature absorption spectrum of t-BuNO is shown in Fig. 2, along with the laser fluorescence excitation spectrum. The overall features revealed are similar to those observed in CF_3NO [5,6,8] but the quantum yield of the fluorescence is apparently much lower: At laser wavelengths > 695 nm, where the excitation spectrum closely resembles
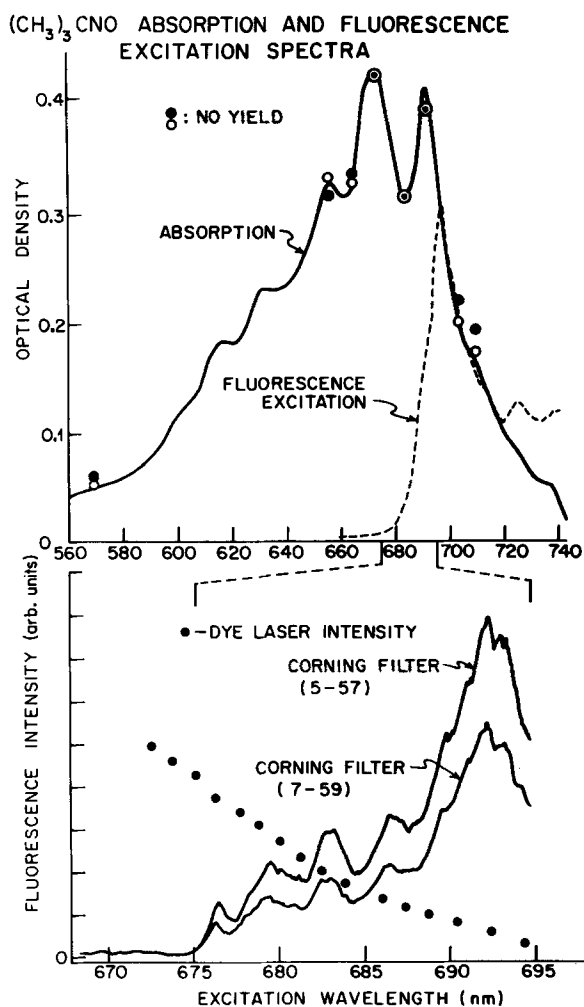
$(CH_3)_3CNO$ ABSORPTION AND FLUORESCENCE EXCITATION SPECTRA

FIG. 2. Absorption and fluorescence excitation spectra of t-BuNO at low resolution (1 nm). The absorption spectrum was obtained with 60 Torr of t-BuNO. The fluorescence excitation spectrum was obtained with 0.5 Torr of t-BuNO, and is normalized to the laser intensity and to the absorption spectrum at 697.5 nm. NO relative yields, normalized to the absorption spectrum at 670 nm, are also indicated in the upper panel. They were obtained at 200 mTorr pressure and a delay of 30 ns. In the lower panel, two scans of a portion of the fluorescence excitation spectrum at a higher resolution (1 cm^{-1}) are shown. The spectrum is not corrected for changes in the laser energy which is also shown.

the absorption spectrum, the fluorescence intensity per absorbed photon is about 0.02 that of CF_3NO. In addition, at wavelengths < 695 nm there is a dramatic decrease in fluorescence intensity. As can be seen from the lower panel of Fig. 2, which shows high resolution spectra taken in the region 670–695 nm, the same qualitative results were obtained with a Corning 5-57 filter (720 nm cutoff) and a Corning 7-59 filter (695 nm cutoff). It is thus unlikely that the sharp intensity decrease is due to a spectral shift in emission spectrum upon variation of the excitation wavelength. We have not been able to measure accurately the fluorescence lifetimes, which, even with 730 nm excitation, are ≤ 20 ns, because of the limited response time of our detection system and the low signal intensities.

As in the work on CF_3NO,[8(b)] we have attempted to

induce collisional relaxation of vibrational levels of the excited S_1 state of t-BuNO to its ground vibrational level, so that the absorption and emission spectra would become similar. However, the addition of 200 Torr of SF_6 to the t-BuNO sample caused attenuation of the signal amplitude at all wavelengths, to the point where it was impossible to carry out the measurements.

B. NO production

Production of NO, as indicated by the appearance of a TPEF signal, was readily observed over the wavelength range 570–710 nm. A representative TPEF spectrum is shown in Fig. 3. The spectrum looks very similar to the room temperature spectrum of pure NO obtained at the same resolution,[13,14] and based on analysis of the well resolved O_{12} lines,[15] a temperature of 300 K is obtained. Since the spectrum was obtained at 2 Torr pressure and 100 ns delay between the photolysis and the probe lasers, it is rotationally relaxed, and therefore should be 300 K. A spectrum taken at 100 mTorr and 20 ns delay was very similar in the 452–453 nm region, but owing to the low intensity of the O_{12} lines, an exact value for the rotational temperature could not be obtained at low pressure. However, the spectrum looks much cooler than the 900 K spectrum reported for NO from CF_3NO.[7(b)] Low rotational excitation of NO was also obtained in the dissociation of t-BuNO following 532 nm excitation.[16]

At a fixed photolysis laser energy, the relative yield of NO (determined from the intensity of the $P_{11} + O_{21}$ bandhead) was found to vary in accordance with the t-BuNO absorption contours. This can be seen in Fig. 2, where the NO yields are normalized to the absorption peak at 670 nm. Although the fluorescence yield from t-BuNO was much smaller than that from CF_3NO, the NO yields from both precursors were similar, indicating that predissociation is the major decay channel for t-BuNO, as it is for CF_3NO.[7(b)] The NO appearance time at all excitation wavelengths measured (570–710 nm) was very fast, and measurements were limited by the time resolution of our experiments (10 ns). Thus, the dissociation rates, even at the longest wavelength used, are faster than 10^8 s^{-1}. Typical rise and decay curves are shown in Fig. 4. They were obtained by varying the delay between the photolysis and probe laser pulses, using a digital delay generator with delay increments of 10 ns. The rise times did not vary with pressure in the range 50–1000 mTorr. The decay times, which are determined mainly by movement out of the interaction zone, were strongly dependent on the pressure and the f. l. of the lens used with the photolysis laser, since this determines the waist at the focus. As expected, decay times ranged from ~1 μs at 100 mTorr with a 15 cm f.l. lens to > 10 μs at 1 Torr with a 100 cm f.l. lens.

Several checks were made to verify that the contributions to the observed rise times of two-photon excitation of t-BuNO, and of collisional effects, were negligible. The NO TPEF signal increased linearly with photolysis laser energy for all focusing lenses used (Fig. 5), and the NO TPEF signal increased linearly with t-BuNO pressure between 0.05 and 0.5 Torr. At higher pressures,
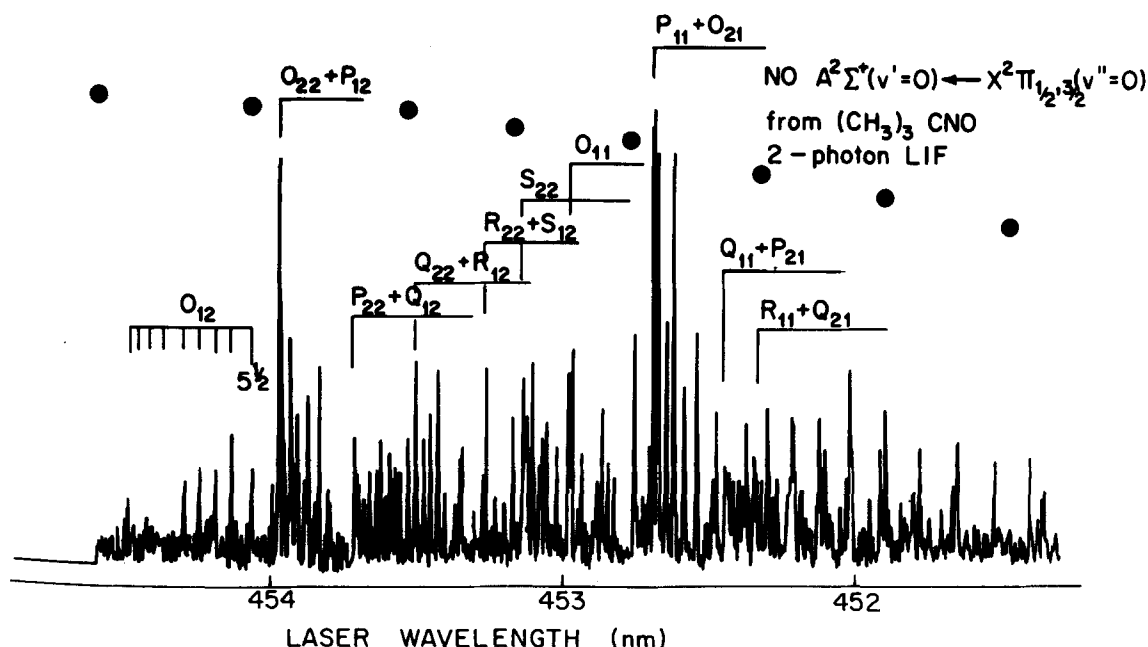
FIG. 3. The TPEF spectrum of NO produced by photolysis of 2.0 Torr t-BuNO at 670 nm, 100 ns after excitation. The relative intensity of the probe laser used to obtain the TPEF spectra is also shown as a function of wavelength.

IV. DISCUSSION

The most significant result of the present study is the observation of t-BuNO dissociation rates, which are faster than those deduced from the thermal activation unimolecular rate measurements.[10] As this conclusion relies on a quantitative comparison between the measured NO appearance rates, and dissociation rates derived from thermal data and the RRKM formalism via Eq. (1),[11,12] a closer scrutiny of the assumptions and errors involved in the use of this equation is in order. A detailed discussion has been given by Forst,[11,12] and therefore, only the features salient to our results will be summarized here.

Equation (1), while mathematically exact, is based on the increase in signal was less than linear due probably to quenching of NO fluorescence by t-BuNO.

the assumption that the high pressure unimolecular rate coefficient k_∞ can be described by

$$k_\infty = A_\infty \exp(-E_{a\infty}/kT) , \qquad (2)$$

which is, of course, valid only over a limited temperature range. The major error sources in k_∞ are experimental errors in A_∞ and $E_{a\infty}$. The values we used were derived from measurements using the very low pressure pyrolysis (VLPP) technique,[10] which is rather reliable. Nevertheless, the combined errors in $E_{a\infty}$ and A_∞ are magnified in $k'(E)$, as can be seen in Fig. 1, which shows results derived from the average values given in Ref. 10, and also from their limiting values. It was also shown,[12] that the near threshold $k'(E)$ values obtained from Eq. (1) are sometimes higher than those derived directly from an RRKM model, which is based on assuming a structure for the transition complex. However, as Forst points out,[12] since both treatments
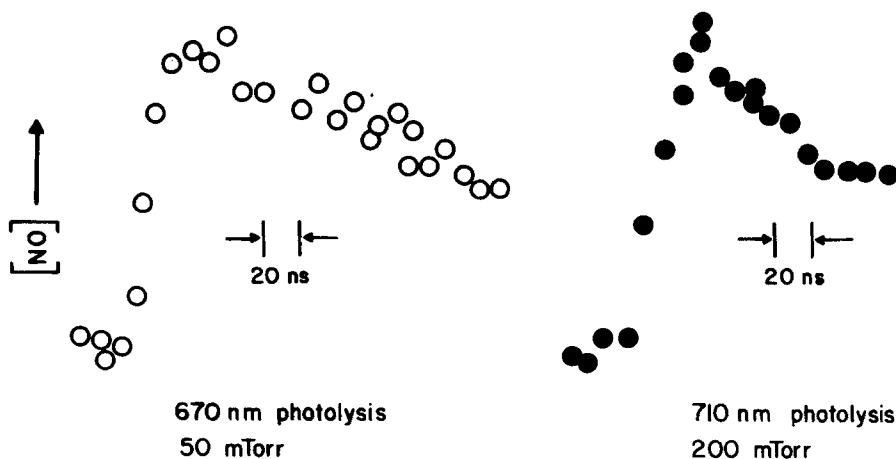

FIG. 4. Appearance time of NO $(v'' = 0)$ TPEF signal at two photolysis wavelengths.

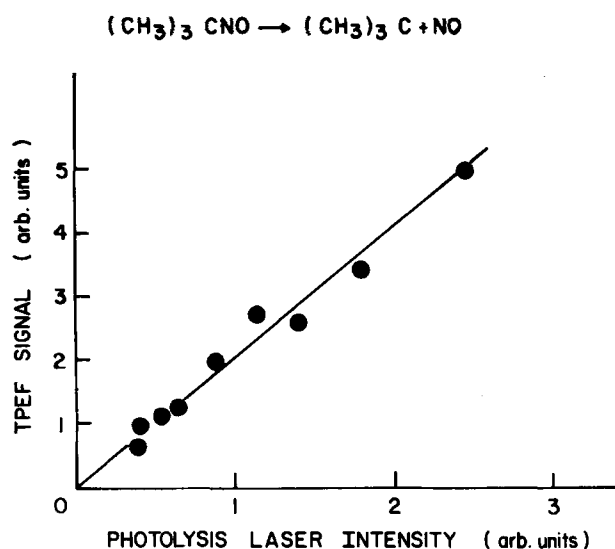$$(CH_3)_3\ CNO \longrightarrow (CH_3)_3\ C + NO$$

FIG. 5. NO $(v'' = 0)$ TPEF signal as a function of photolysis laser intensity obtained following excitation at 670 nm at 30 ns delay. The photolysis laser output was focused using a 100 cm focal length lens. The pressure was 500 mTorr.

rely on assumptions and imperfect experimental information, it is impossible to determine which is more "correct." Forst concludes that the $k'(E)$ of Eq. (1) represents all the limited information that can be extracted from thermal data. The main advantage in its use is that no structure for the transition state need be assumed, and therefore, there are no parameters to adjust.

We have checked other possible sources of error in the calculation of $k'(E)$ using Eq. (1). The vibrational frequencies of t-BuNO, which are not known exactly, were deduced from IR spectra[17,18] and compared with those of t-butyl halides[19] and the t-butyl radical.[20] Varying the values of the low bending vibrations of t-BuNO within reasonable limits did not change $k'(E)$ significantly. Likewise, using the Whitten–Rabinovitch approximation,[11,21,22] or a direct count of vibrational states with the grouped frequency model[21,22] gave comparable densities of states. Ignoring the mild temperature dependence of the centrifugal factor f_∞[11] is also of minor importance.

Thus, we conclude that the major sources of uncertainty in $k'(E)$ derive from A_∞ and E_{∞}, and therefore, the range of values shown in Fig. 1 depicts the anticipated rate coefficients based on the thermal data.[10] The rates $k'(E)$ could be reproduced very nicely over the excess energy range shown in Fig. 1 using the RRKM model,[22] with a transition state in which four low bending vibrations were reduced by factors of 2–5 from their original values. This is very reasonable for a simple bond fission reaction.[11,21]

The largest uncertainty in the comparison of our results with the thermal rate data derives from the uncertainty in the calculation of the excess energy E^* which is given by

$$E^* \cong E_{h\nu} + \langle E_v \rangle - E_{diss}, \qquad (3)$$

where $E_{h\nu}$ is the energy of the exciting photon, $\langle E_v \rangle$ is

the average vibrational energy content of t-BuNO at room temperature $(2.5 \pm 0.5\ \text{kcal mol}^{-1})$, and E_{diss} is the bond dissociation energy of t-BuNO $\rightarrow$ t-BuNO + NO.

Two different values of E_{diss} have been reported to date. The value derived from the thermal rate data is $39.5 \pm 1.5\ \text{kcal mol}^{-1}$,[10] while the value determined mass spectrometrically is $34 \pm 3\ \text{kcal mol}^{-1}$.[23] A similar discrepancy existed for CF_3NO, where the kinetically derived value of $42 \pm 2\ \text{kcal mol}^{-1}$[24] is high compared to the mass spectrometric value of $31 \pm 3\ \text{kcal mol}^{-1}$.[25] The observation of $NO(v = 3)$ in Ref. 7(b) was cited as proof that the bond energy in CF_3NO was $< 33\ \text{kcal mol}^{-1}$. However, more recent results indicate that the higher vibrational levels of NO were produced by a two photon absorption process, and analysis of the rotational temperatures of NO obtained following excitation of CF_3NO in a supersonic beam shows good agreement with the higher value.[26] In the case of t-BuNO, the mass spectrometric value was based on the difference between the appearance potential (AP) of the t-butyl radical from t-BuNO and its ionization potential (I. P.).[23] The value assumed for the I. P. of the radical was 7.43 eV, whereas more recent measurements give a value of 6.95 ± 0.05 eV.[27-29] Using this latter value and an AP of the t-butyl radical from t-BuNO of 8.9 ± 0.1 eV,[23] the resultant value for the bond dissociation energy becomes $46 \pm 3\ \text{kcal mol}^{-1}$. This is an unrealistic value, since we observe rapid dissociation following 710 nm photolysis of t-BuNO, where the available energy $E_{h\nu} + \langle E_v \rangle$ is only $42.7 \pm 0.5\ \text{kcal mol}^{-1}$. Thus, we prefer the value given in Ref. 10. This value leads to $E^* = 3.2 \pm 2\ \text{kcal mol}^{-1}$ for 710 nm photolysis which, according to Fig. 1, corresponds to an upper limit on the dissociation rate of $6 \times 10^6\ \text{s}^{-1}$, and to a most likely value of $1.5 \times 10^6\ \text{s}^{-1}$. Only at $E^* > 12\ \text{kcal mol}^{-1}$ could the dissociation rate exceed $10^8\ \text{s}^{-1}$.

We also point out a very recent study of the dissociation of t-butylhydroperoxide $(t$-BuOOH) following direct excitation of overtone vibrations of its ground state.[2] The thermal dissociation rate parameters of t-BuOOH are quite similar to those of t-BuNO $(A_\infty = 10^{15.6}\ \text{s}^{-1}$, $E_{\infty} = 43\ \text{kcal mol}^{-1})$,[30] and so are the structures of the molecules, and the numbers of degrees of freedom. In the overtone excitation experiment, a dissociation rate of $4 \times 10^6\ \text{s}^{-1}$ was observed at an excess energy of ~12 kcal mol^{-1}.

We thus conclude that the appearance time of NO from t-BuNO following 710 nm excitation cannot be explained by statistical theories of unimolecular decay from the ground electronic state.

Several dissociation mechanisms could account for the fast appearance times of NO:

(a) Direct excitation to a repulsive state, (b) vibrational predissociation from the excited S_1 state, (c) dissociation following fast IC to S_0, without randomization of vibrational energy in S_0, (d) dissociation following intersystem crossing between S_1 and the lowest triplet state T_1, and (e) dissociation following crossing from S_1 to a repulsive surface.

In discussing the various possible mechanisms, we take advantage of the fact that the lowest electronic

states of alkyl nitroso compounds are rather similar, since they all derive from a similar transition of a non-bonding electron centered on N to an antibonding π^* orbital.[5] Thus, we can safely assume, based on calculations carried out for the prototypical HNO molecule,[31-35] that the electronic states which lead to ground state dissociation products are, in ascending order, $S_0(^1A')$, $T_1(^3A'')$, $S_1(^1A'')$, $^3A'$ and $^1A'$, the latter two being repulsive states. However, the locations of the minima, and the locations and heights of possible barriers in t-BuNO cannot be inferred from HNO calculations, since the details of the molecular orbital interactions in HNO and t-BuNO are different.

Although we cannot determine the predissociation mechanism(s) from our data, several routes can be excluded. Direct excitation to a repulsive state [mechanism (a)] is ruled out by the observation of fluorescence from the S_1 state, and by the fact that the $NO(v=0)$ yield follows closely the n-π^* absorption contours in the region 570–710 nm.

Mechanism (b) is also very unlikely. The observation of fluorescence at wavelengths above dissociation threshold implies a barrier to dissociation from the S_1 state, whereas we observe efficient NO production at wavelengths where fluorescence is observed, and thus excitation to levels below the barrier must have occurred. Had there been no barrier, our RRKM calculations show that the dissociation rate would be too fast to allow observation of a competing fluorescence channel. Tunneling through a barrier is insignificant for heavy molecular fragments such as t-Bu and NO.

Mechanism (c) involves dissociation from the ground state without prior randomization of energy. Based on their calculations of CF_3NO optical excitation, Spears and Hoffland[8(b)] indicate that the ground state vibrational energy distribution in CF_3NO immediately following a radiationless transition from S_1 should be dominated by NO stretching motions. If such NO stretching motions are subsequently coupled directly to the C–NO bond, they may cause dissociation without complete energy randomization in the CF_3 radical.[36] We do not have any experimental evidence either to support or refute such a mechanism in t-BuNO.

Both mechanisms (d) and (e) are compatible with our experimental observations. The lowest triplet state of t-BuNO, T_1 is apparently lower in energy than S_1, and our RRKM calculations indicate (assuming that the structure of the T_1 and S_0 transition states are similar) that a triplet state lying at $\gtrsim 10$ kcal mol^{-1} above S_0 would lead to a dissociation rate of $>10^8$ s^{-1} following 710 nm excitation. A crossing between S_1 and a repulsive state cannot be precluded either. Such a crossing is not indicated in *ab initio* calculations of HNO. However, these calculations[32-35] do not always agree with each other, and, moreover, HNO potential surfaces are not expected to show quantitative resemblances to those of t-BuNO. We also point out that more than one mechanism may be responsible for the NO appearance, and that the contributions of the different mechanisms may change as a function of the photolysis wavelength.

Finally, we would like to comment on the dramatic

decrease in the fluorescence yield following excitation at $\lambda < 695$ nm (Fig. 2). By comparing with CF_3NO, whose fluorescence quantum yield near the origin is less than 1%, we find a quantum yield of $\sim 10^{-4}$ for t-BuNO, even at the longest excitation wavelengths. Using 10 μs as an estimate for the radiative lifetime,[8] the radiationless transition rate is $\sim 10^9$ s^{-1}, and hence the fraction of molecules that fluoresce and do not dissociate is very small indeed. Further increase in the radiationless transition rate with decreasing wavelength would cause a decrease in the fluorescence quantum yield, without significantly affecting the NO yield. At short wavelengths (<695 nm) higher vibrational levels in S_1 are excited, which may have faster radiationless transition rates than the lower vibrational levels excited at longer wavelengths. In addition, at room temperature, absorption occurs from a range of vibrational levels in S_0, and hence the fraction of absorbing molecules that reach high vibrational levels in S_1 increases with the decrease in wavelength, contributing to the sharp decrease in fluorescence yield.

An alternative explanation, the onset of an additional direct dissociation from the S_1 surface following excitation to levels above the barrier, could lead (based on RRKM calculations) to a much faster and abrupt decrease in the fluorescence yield than is observed. However, since at room temperature absorption occurs from a range of vibrational levels in S_0, the fraction of absorbing molecules that reach vibrational levels in S_1 which are above the barrier varies with wavelength, and as a result the decrease in fluorescence yield can be spread over a significant wavelength range. Therefore, this mechanism cannot be ruled out. Experiments with supersonic nozzle expansions, where most of the molecules are at low vibrational levels, will help distinguish between the two mechanisms.

V. CONCLUSIONS

In this study we show that the lifetime of t-BuNO excited to the $S_1(^1A'')$ state is controlled by fast, radiationless processes which lead to efficient dissociation to t-Bu + NO. The appearance time of NO is not compatible with a dissociation mechanism whereby the excited t-BuNO undergoes fast IC to the ground electronic state S_0 followed by complete energy randomization and dissociation. Predissociation via crossing to a repulsive state, and/or intersystem crossing to the lowest triplet state are possible alternatives.

In the present experiments, measurements of NO appearance times near the origin of the n-π^* transition, and of energy disposal in NO as a function of the excitation level were hindered because of the thermal internal energy content of t-BuNO, and the resultant lack of structure in the absorption spectra. As in the case of CF_3NO, the spectra in a supersonic beam should be greatly simplified, and state-selective photolysis studies, especially near threshold, should become possible.[8(c),37] We are currently introducing a pulsed molecular valve into our experimental arrangement for such studies.

In addition, comparisons with dissociation rates fol-

lowing IR multiple photon excitation of t-BuNO should be very illuminating since, in this case, dissociation proceeds from the ground state manifold. Weak IR absorption features around 940 and 1030 cm^{-1} may be used to induce the dissociation.[18]

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