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Rate Coefficients for the H + NH₃ Reaction over a Wide Temperature Range

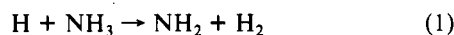
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The temperature dependence of the rate coefficients for the H + NH₃ → NH₂ + H₂ reaction is measured by the high-temperature photochemistry (HTP) technique. Technique improvements are discussed. For the 490–960 K range, we find $k_1(T) = 1.21 \times 10^{-10} \exp(-6920 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. When combined with two other sets of direct measurements, a best fit gives $k_1(T) = 9.0 \times 10^{-19} (T/\text{K})^{2.40} \exp(-4991 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the 490–1780 K range. It is shown that these data can be more closely fitted by a calculation based on conventional transition-state theory plus an Eckart tunneling model than with other current transition-state models considered. Using the potential energy surface for the H + NH₃ reaction, several tunneling models fit the results for the D + ND₃ reaction. The kinetic isotope effect for these two reactions is compared to results from different theoretical models, with the Eckart model giving the best approximation.

Introduction

Rate coefficients for the elementary reaction



have recently been measured by three groups^{1–4} using different isolated elementary reaction techniques. Marshall and Fontijn¹ used the high-temperature photochemistry (HTP) technique over the 500–1140 K range, Michael et al.² made flash-photolysis shock-tube (FP-ST) measurements from 900 to 1780 K, while Hack et al.³ used a discharge flow reactor (DFR) for the 670–1000 K regime. The results in the overlapping temperature ranges agree within the error limits. However, the data below 650 K reveal a stronger curvature, i.e., leveling off with decreasing temperature, than could quantitatively be described either by conventional (CTST)^{1,2,5} or by variational transition-state theory (VTST)⁶ calculations. In addition, when k_1 values from the HTP work are combined with extrapolated values of k_{-1} from Hack et al.,³ some irregular behavior of $\ln K_{\text{eq}}(T)$ vs T^{-1} was noted.⁷ Although the latter may not be disturbing in view of the combined scatter and the extrapolation involved, a redetermination of k_1 was prompted. This work has yielded significantly higher values around 700 K but reproduced our earlier results nearer the upper and lower temperatures. The possible reasons for this, i.e., procedural improvements, are discussed.

Experimental Technique

The basic experimental equipment, method, and data handling procedures of this work were essentially the same as employed in our earlier work.¹ Ground-state H atoms were generated by flash photolysis of NH₃, using the radiation of an N₂-filled lamp filtered through a Suprasil quartz lens ($\lambda > 160 \text{ nm}$). The atom concentration was monitored by time-resolved resonance fluorescence with pulse counting and signal averaging. The operational procedures, however, have improved with time and experience. In view of the differences in results mentioned above, these improvements deserve some description.

Residence time requirements for $\geq 95\%$ mixing for a point source were calculated and strictly obeyed here, though actual mixing from the 0.64-cm-diameter opening of the cooled-inlet tube (Figure 1) is faster than indicated by those calculations.⁸ Previously, the upper and lower helical SiC heating elements were resistively heated in parallel, with one variable autotransformer. As more recently noticed, this could have led to a temperature at the upper (downstream) edge of the observed, about 1.3 cm long, reaction zone higher by as much as 25–30 K than at the lower edge. In the present work each heating element was powered by its own autotransformer hence allowing independent control. An off-axis fixed chromel–alumel (Type K) thermocouple (TC) in a stainless steel housing was added to each section to allow the

temperature 2.5 cm above and below the center of the observation window (PMT) to be equalized. Under these conditions, the temperature at the center of the observed zone was less than 5 K lower than at its up- and downstream edges. Additionally, the presence of these extra TCs gives a check on the performance of the axial radiation-shielded^{14,15} Pt–Pt/13% Rh (Type R) retractable TC (Figure 1), which is used to measure the temperature of the observed reaction zone before and after each kinetic experiment. The junction of this TC is covered with alumina paste.

The 99.998% NH₃ was previously¹ used without further purification but in the present work was subjected to three freeze-pump-thaw cycles using ethanol slush at 156 K.

Experimental Results

The present 44 measurements of k_1 in the 490–960 K range are summarized in Table I together with the following experimental parameters: total pressure, P ; total concentration, $[M]$; average linear gas velocity, \bar{v} ; inlet-to-reaction zone distance, z ; and flash energy, F . No apparent dependence of k_1 was observed for about 10-fold changes of those parameters. The uncertainties in the temperatures, σ_T , and the rate coefficients, σ_k , were assessed as described previously.^{1,5,8} Taking into account both σ_T and σ_k , the present data are well fitted in the Arrhenius form $k(T) = A \exp(-E \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by

$$k_1(T) = 1.21 \times 10^{-10} \exp(-6920 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (2)$$

for which the variances⁹ and the covariance¹⁰ are $\sigma_A^2 = 6.6 \times 10^{-22}$, $\sigma_E^2 = 2.2 \times 10^4$, and $\sigma_{AE} = 3.6 \times 10^{-9}$. The 2σ precision level of the fit is better than 14%. After allowing conservatively 20% for possible systematic errors, 95% confidence limits are estimated at $\pm 25\%$.

These measurements of k_1 are in good agreement with the previous HTP results¹ in the upper and lower regions of the investigated temperature range. However, in the 600–850 K range the current values are larger. The difference is by as much as a factor of 3 at around 700 K. The cause of these differences has been investigated by including, in the present data set, a few experiments in which the conditions of the earlier work were mimicked. As may be seen from Table I, neither the temperature gradient nor the purification of NH₃ has any discernible influence on the results. Additionally, an examination of the earlier data

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TABLE I: Summary of Rate Coefficient Measurements on H + NH₃

$T, ^\circ\text{K}$	$P, ^b\text{Torr}$	$[\text{M}], 10^{18}\text{ cm}^{-3}$	$[\text{NH}_3], 10^{15}\text{ cm}^{-3}$	$\bar{v}, \text{ cm s}^{-1}$	$z, \text{ cm}$	$F, \text{ J}$	$k \pm \sigma_k, \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
486	210	4.1	13-160	5.8	47 ^c	35	1.11 ± 0.11 (-16) ^d
491	540	11	15-210	4.8	47	17	9.40 ± 0.70 (-17)
498	100	1.9	23-130	5.9	47	59	1.08 ± 0.15 (-16)
506	230	4.3	21-160	5.4	47	50	1.53 ± 0.12 (-16)
510	210	3.9	12-120	6.1	47	59	1.89 ± 0.24 (-16)
520	330	6.1	17-110	6.8	47	50	2.31 ± 0.17 (-16)
532	310	5.6	11-150	5.5	15	50	2.47 ± 0.42 (-16)
532	310	5.6	16-150	5.4	47	7	2.43 ± 0.25 (-16)
536	410	7.3	11-160	5.6	47	17	3.23 ± 0.39 (-16)
545	260	4.5	13-150	5.5	47	50	3.43 ± 0.11 (-16)
562	100	1.7	8.5-63	11	21	22	6.68 ± 0.50 (-16)
569	260	4.4	12-81	5.6	21	35	5.83 ± 0.70 (-16)
583	260	4.2	23-99	5.8	47	50	6.25 ± 0.66 (-16)
585	260	4.3	16-100	5.8	47	59	7.30 ± 0.20 (-16)
591	260	4.2	21-100	5.9	47	7	8.65 ± 0.50 (-16)
603 ^f	240	3.8	15-77	8.1	15	35	7.71 ± 0.15 (-16)
614 ^f	230	3.6	1.8-56	8.4	15	35	1.11 ± 0.06 (-15)
622	470	7.2	15-74	6.4	21	22	1.68 ± 0.05 (-15)
633 ^e	230	3.6	3.1-17	8.6	10	22	2.58 ± 0.07 (-15)
638	250	3.8	12-70	6.3	47	35	2.12 ± 0.08 (-15)
647	110	1.6	5.5-31	19	15	35	3.39 ± 0.22 (-15)
651	310	4.6	11-36	6.6	15	50	2.78 ± 0.02 (-15)
673 ^f	190	2.7	4.9-36	3.3	8	50	3.49 ± 0.33 (-15)
678 ^f	110	1.5	5.7-30	20	15	22	3.49 ± 0.06 (-15)
682 ^f	110	1.5	1.7-26	4.8	15	40	3.44 ± 0.17 (-15)
683 ^f	110	1.5	4.8-24	21	15	22	3.99 ± 0.10 (-15)
703	170	2.3	4.7-16	13	15	35	8.36 ± 0.52 (-15)
713	480	6.4	9.3-65	6.8	8	5	6.29 ± 0.47 (-15)
742 ^e	230	3.0	2.9-37	10	10	50	1.11 ± 0.05 (-14)
746 ^f	210	2.7	2.5-14	11	8	50	8.48 ± 0.70 (-14)
753	52	0.66	1.7-7.3	20	15	17	1.52 ± 0.19 (-14)
753	52	0.66	1.7-7.3	20	15	59	1.60 ± 0.06 (-14)
760	95	1.2	2.9-15	24	10	50	1.56 ± 0.18 (-14)
774 ^f	120	1.5	2.1-16	10	8	40	1.40 ± 0.05 (-14)
798	110	1.3	1.8-11	32	21	50	2.74 ± 0.28 (-14)
805 ^f	85	1.0	0.8-6.2	30	8	40	1.89 ± 0.10 (-14)
825 ^e	230	2.7	1.9-10	11	4.0	50	2.82 ± 0.04 (-14)
868	460	5.1	1.8-12	8.2	8.0	22	3.98 ± 0.36 (-14)
869	51	0.56	1.3-6.2	24	15	35	3.06 ± 0.17 (-14)
871	50	0.55	0.6-5.5	24	7.0	35	4.61 ± 0.51 (-14)
874	220	2.4	1.0-5.1	17	10	35	5.14 ± 0.59 (-14)
951	350	3.6	1.0-5.1	19	15	35	8.40 ± 0.17 (-14)
955	350	3.6	1.4-6.6	19	8.0	35	9.51 ± 0.55 (-14)
956	350	3.6	1.2-6.8	19	21	35	7.08 ± 0.24 (-14)

^a $\sigma_T/T = 2\%$. See ref 1. ^b1 Torr = 133.3 Pa. ^c $z = 47$ cm corresponds to premixing of the reactant and bath gases; the cooled inlet was not used. ^dShould be read as $(1.11 \pm 0.11) \times 10^{-16}$. ^eNH₃ was used directly from cylinder. ^fNH₃ was used directly from cylinder, and temperature gradient was similar to that in the work of ref 1.

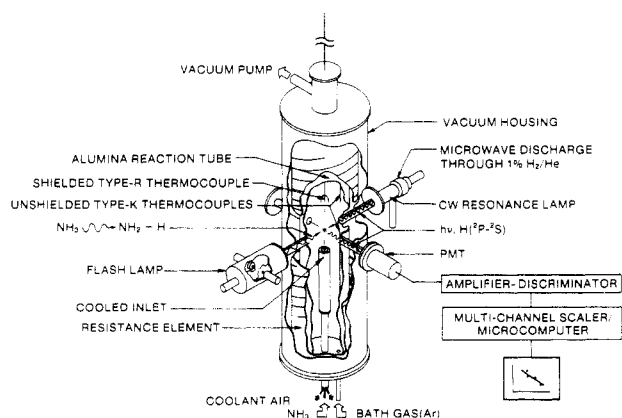


Figure 1. Schematic of the HTP reactor as used.

shows that all but three measurements met the residence time requirement for 95% mixing. Those points at 975, 914, and 860 K lie outside the temperature range where that and the present data set differ and do not deviate from the k_1 values indicated by the neighboring measurements. Thus, we cannot point to one or more specific factors as being responsible. Neither is it clear why the data around 700 K should have been particularly affected. Rather, the combination of changes, made since the first study

with the reactor design involved, i.e., since the work of ref 1, has led to improved data. Of these steps the prevention of a temperature gradient and the ready check on thermocouple performance, provided by the TCs up- and downstream of the observed reaction zone, must be considered particularly important.

In Figure 2, the present HTP results are compared with the results of the other two groups. Comparison with the data of Michael et al.² shows close agreement in the region of overlapping temperature, 900-960 K, as does their single point using the flash-photolysis resonance-fluorescence (FP-RF) method at 750 K. The best-fit expression of Hack et al.³, $k_1(T) = 1.35 \times 10^{-10} \exp(-7330 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, falls slightly below that of the present work, though several of their seven individual measurements may be seen to overlap with the present results.

In view of the good agreement in the experimental data, a best fit can be determined by combining the present data set with those of Michael et al. and Hack et al. To generate a combined data set, we calculate k_1 values at 50 K intervals from the best-fit expressions of these three investigations in their respective temperature ranges. This yields

$$k_1(T) = 9.00 \times 10^{-19} (T/\text{K})^{2.40} \exp(-4991 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (3)$$

for $490 < T < 1780 \text{ K}$.¹¹ Confidence limits are not calculated

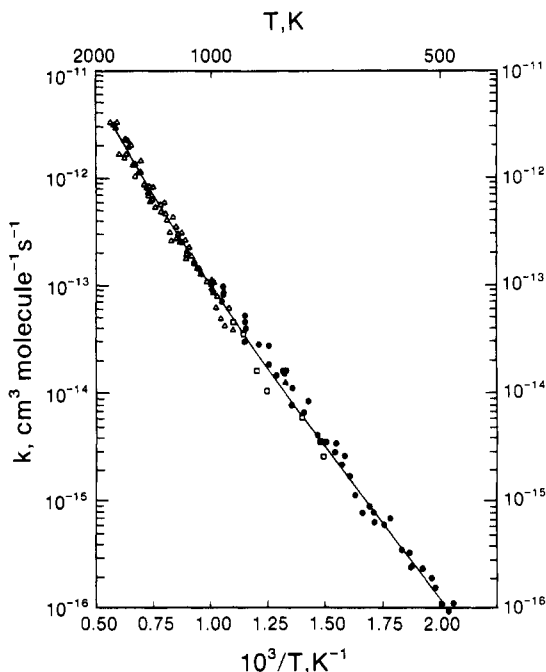


Figure 2. Plot of rate coefficients for the H + NH₃ reaction: present work (●); Michael et al.² by FP-ST (Δ); Michael et al.² by FP-RF (▲); Hack et al.³ by DFR (□); best fit (—) to all these data.

for this best-fit expression due to insufficient information on accuracy but may be estimated to be similar to those of eq 2. Equation 3 is shown as the solid line in Figure 2. Although none of the individual studies reveal any significant non-Arrhenius behavior, the combined data set indicates curvature in the $\ln k_1(T)$ vs T^{-1} plot. We note that Michael et al.² on the basis of a hint of curvature in their data alone derived a three-parameter fit that is similar to eq 3.

Discussion

In Figure 3, VTST and CTST theoretical estimates of $k_1(T)$ are compared with the experimental best fit. The calculation using ICVT/SCSAG, a form of VTST combined with a multidimensional tunneling model, is from Garrett et al.⁶ The CTST calculations presented here are based on a method essentially identical with that used earlier,⁵ employed in three ways. First, quantum-mechanical tunneling is neglected (CTST/N), second, Wigner tunneling is assumed (CTST/W),¹ and third, Eckart tunneling is considered (CTST/E).^{1,8,12} The energy barrier E_0 in each case is empirically determined by requiring the calculated $k_1(950\text{ K})$ to agree with the value from eq 3. A temperature of 950 K is chosen because there (i) any tunneling is only weakly dependent on E_0 and (ii) the three data sets, included in the best fit, overlap. This yields E_0 values of 59.7, 63.5, and 65.0 kJ mol⁻¹ for CTST/N, CTST/W, and CTST/E, respectively. The Eckart tunneling calculations are for an asymmetric barrier where the reverse barrier height of 50 kJ mol⁻¹ is obtained from the forward barrier height and the heat of reaction, $\Delta H^\circ_0 = 15\text{ kJ mol}^{-1}$.^{7,13} It can be seen from Figure 3 that ICVT/SCSAG calculations, where E_0 is derived ab initio rather than empirically, underestimate the rate coefficients systematically. Garrett et al. have noted that this indicates a systematic overestimation of the free energy of activation in their calculations.⁶ For CTST/N and CTST/W,

(11) Using instead $1000/T = 0.1\text{ K}^{-1}$ intervals or weighting according to the number of independent rate measurements gave essentially indistinguishable fits.

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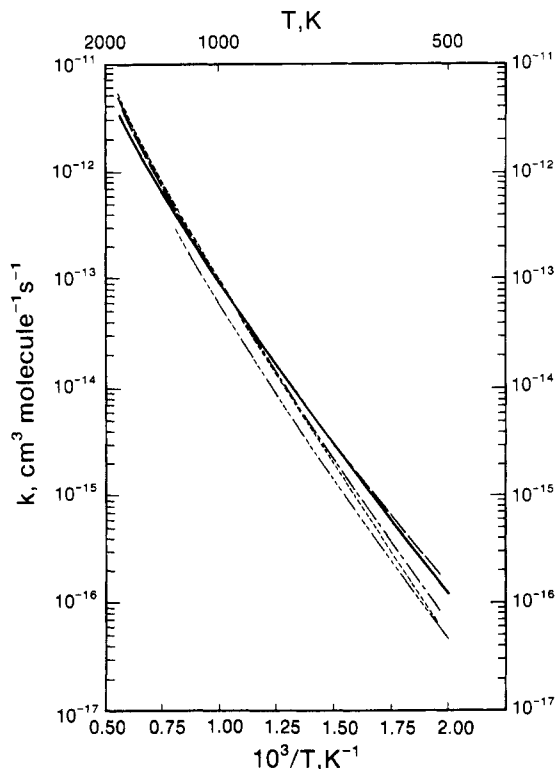


Figure 3. Comparison of experimental and model $k_1(T)$ values: experimental best fit (—); ICVT/SCSAG (-----); CTST/N (---); CTST/W (-.-); CTST/E (---).

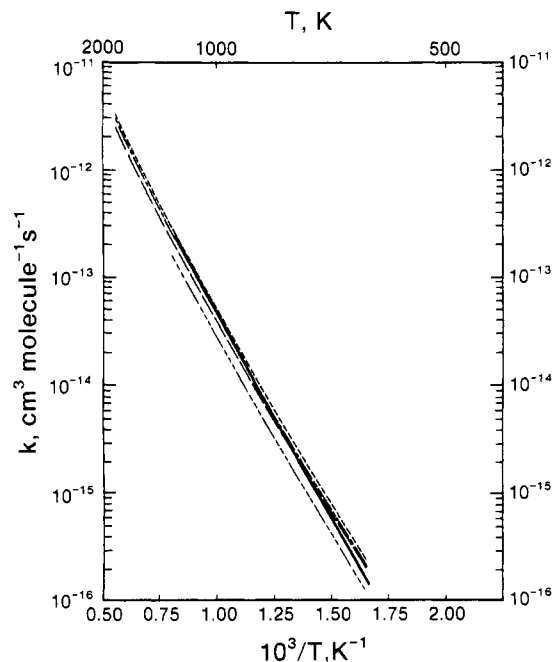
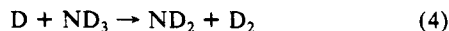


Figure 4. Comparison of experimental⁵ and model $k_4(T)$ values: experimental best fit (—); ICVT/SCSAG (-----); CTST/N (---); CTST/W (-.-); CTST/E (---).

the levels of agreement with eq 3 are no worse than about $\pm 60\%$ and $\pm 50\%$, respectively. An interesting point there is the consistent overestimation above about 950 K and consistent underestimation below 950 K. Such a diverging trend is not present in the results from CTST/E where the agreement is within $\pm 27\%$ or better over the 490–1780 K range.

We have also carried out a similar set of theoretical studies for the reaction



for which $\Delta H^\circ_0 = 18\text{ kJ mol}^{-1}$, using the same potential energy

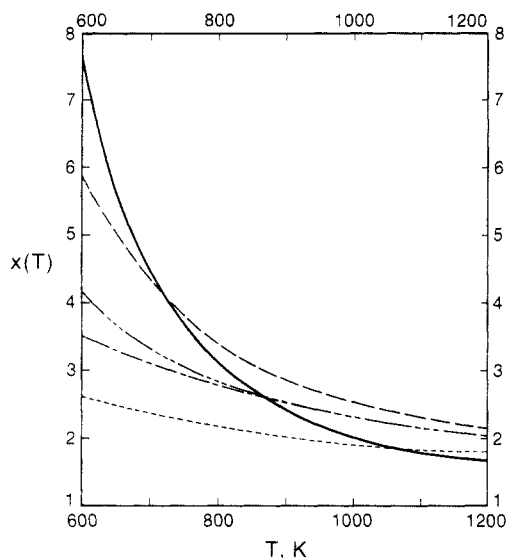


Figure 5. Comparison of the kinetic isotope effect $x(T) = k_1(T)/k_4(T)$ between experimental and models: experimental best fit (—); ICVT/SCSAG (-----); CTST/N (-.-.); CTST/W (---); CTST/E (---).

surface as for reaction 1 and making changes based only on mass and zero-point energy differences.⁵ The results are shown in Figure 4. In the 590–1220 K range, the agreement with the experimental $k_4(T)$ of Marshall and Fontijn⁵ is better than $\pm 60\%$ for CTST/N and better than the $\pm 30\%$ error limits of that work for CTST/W and CTST/E. This shows that the tunneling model chosen is not

critical for the transfer of the heavier D atom.⁵ As with reaction 1, ICVT/SCSAG systematically underestimates $k_4(T)$.

In Figure 5, the kinetic isotope effect, $x(T) = k_1(T)/k_4(T)$, from the experimental data and from the four pairs of theoretical calculations is shown. Combining the error limits in $k_1(T)$ and $k_4(T)$ of about $\pm 25\%$ and $\pm 30\%$, respectively, we estimate the confidence limits for the experimental $x(T)$ to be about $\pm 40\%$. Within these error limits, $x(T)$ from the three CTST models agree with the experimental $x(T)$ except for CTST/N at $T < 750$ K and CTST/W at $T < 650$ K. It is interesting to note that although ICVT/SCSAG underestimates $k_1(T)$ and $k_4(T)$ systematically, the $x(T)$ is in good accord in the 650–1220 K range. The closest agreement to the strong curvature in $x(T)$ observed experimentally is from CTST/E.

We conclude that the $\ln k_1(T)$ vs T^{-1} plot does not curve as strongly as our previous results¹ suggested and that both CTST and VTST calculations can approximate the shape of this plot. These experimental data combined with the CTST calculations presented confirm the conclusion reached earlier⁵ that a single potential energy surface and conventional transition-state theory with a simple tunneling model can simultaneously fit the rate coefficients for the H + NH₃ and D + ND₃ reactions.

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Registry No. H, 12385-13-6; NH₃, 7664-41-7; D₂, 7782-39-0.

Anomalous Solvent Effects on the Twisted Intramolecular Charge Transfer Fluorescence of Ethyl 4-(*N,N*-Dimethylamino)benzoate in Chlorinated Solvents

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It was found that the TICT (twisted intramolecular charge transfer) fluorescence of the title compound was very different in chlorinated solvents in comparison with other solvent systems. The emission energy from the a* state (charge transfer state) is higher and the intensity ratio, $R = I_a/I_b$ where I_a and I_b are the emission intensity from the a* state and from the local excited state, is lower at room temperature in CHCl₃ and butyl chloride than in nonchlorinated solvents. The activation energies E_1 and E_2 for the forward ($b^* \rightarrow a^*$) and backward ($b^* \leftarrow a^*$) reactions are also higher in chlorinated solvents. The origin of the anomalous solvent effects was attributed to donor-acceptor type solute-solvent interaction. This interaction was thought to affect the potential energy hypersurface along the reaction path: $b^* \rightarrow a^*$. An anomalous red-shift of the a* band of polymer-bound TICT chromophore in chlorinated solvents was discussed in terms of reduced solvation.

Introduction

Detailed understanding of twisted intramolecular charge transfer (TICT) fluorescence as a function of molecular environment benefits the application of this interesting group of compounds as fluorescence probes. Several reports have already proved the usefulness of TICT compounds as probes for molecular motion in polymers.^{2,3} In the course of studying the title compound (DMABE) as a reference model compound for polymer study, we found anomalous solvent effects on fluorescence in chlorinated solvents.³

The anomaly of TICT fluorescence in chlorinated solvents seems to be a general phenomenon for TICT compounds having dialkylamino groups as electron-donating subunits. Examples are

presented later. The general understanding of solvent effects on TICT fluorescence is as follows. The polarity of the solvent is considered to determine the height of the energy barrier for the $b^* \rightarrow a^*$ process⁴ as well as the stabilization of the a* state, and therefore the emission energy, the relationship between the energy barrier of the TICT formation and solvent polarity, was established.⁵ Solvent viscosity is thought to control the rate of the TICT formation if the process requires no energy barrier.^{6,7}

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