

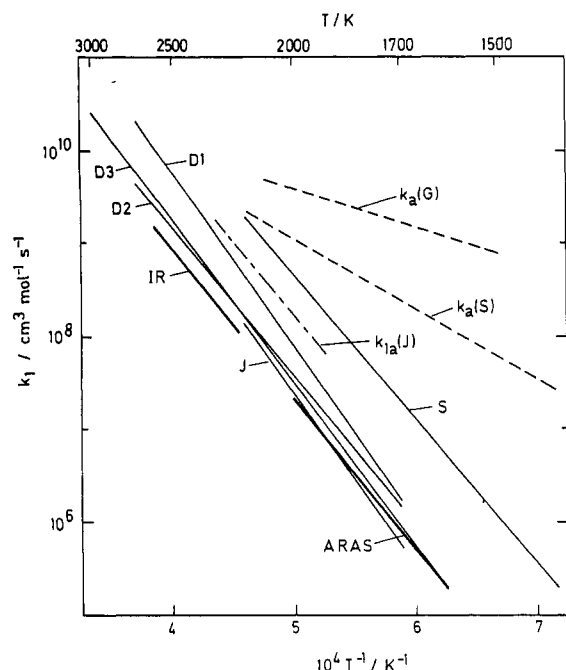


Figure 9. Comparison of the reported rate constants for channel 1. IR and ARAS are the present results obtained by the two methods; S, Schecker and Jost;³ D1 and D2, Dean et al.;⁴ D3, Dean et al.;⁵ J, Just et al.;⁶ $k_a(G)$, apparent rate constant by Gay et al.;² $k_a(S)$, apparent rate constant by Schecker and Jost;³ and $k_{1a}(J)$, channel 1a by Just et al.⁶

For high concentration mixtures, however, the calculated CO curves did not agree with the observed data as shown in Figure 8 for the case of 0.29% mixture. The reason for this large discrepancy is obviously due to assuming the simple mechanism for these mixtures. Therefore, it appears to be necessary to include further secondary reactions in the mechanism to explain all the experimental data. However, if the discussion is limited to highly dilute mixtures, the simple mechanism seems to be enough and the Arrhenius expression for k_1 evaluated from the 4-reaction mechanism appears to be reasonable. This is in essential agreement with the results of the previous workers.⁴⁻⁶ That is, the Arrhenius parameters reported are all in the ranges $\log A = 15.85 \pm 0.35$ and $E_a = 78 \pm 3$ kcal/mol. Figure 9 summarizes the published data and the present results for k_1 in Ar above 1500 K.

B. Rate Constant for Channel 1a. The problem arising from the competing reactions has received a great deal of theoretical and experimental attention as stated above. In the unimolecular

decomposition of formaldehyde the following competing channels have to be considered:²⁴ channel 1, $\text{CH}_2\text{O} + \text{Ar} \rightarrow \text{CHO} + \text{H} + \text{Ar}$ with $\Delta H_{r,0}/\text{kcal mol}^{-1} = 88.7$, and channel 1a, $\text{CH}_2\text{O} + \text{Ar} \rightarrow \text{CO} + \text{H}_2 + \text{Ar}$ with $\Delta H_{r,0}/\text{kcal mol}^{-1} = -0.4$. Channel 1 is a two-center reaction having a loose transition state (TS). Thus the threshold energy E_0 for this channel is thought to be close to the heat of reaction if the centrifugal barrier is neglected. In fact, from photochemical studies^{9,11,13} the energy barrier for this channel was deduced to be in the range 85–88 kcal mol⁻¹. On the other hand, channel 1a is a four-center reaction having a tight TS and is thermochemically neutral. In this type of reaction there is a large energy barrier between reactant and products. According to photochemical studies,⁹ this channel was found to occur by excitation to the S_1 band origin (80.6 kcal mol⁻¹ above the S_0). Recent ab initio calculations for the energy barrier of this channel have given 100,¹⁵ 88.9,¹⁶ 88.4,¹⁷ 83.3,¹⁸ 79.6,¹⁸ and 80.9¹⁹ kcal mol⁻¹, depending on the basis set and on the CI method used. (All values are corrected for the zero-point energy). It is clear that the barrier becomes lower when a larger basis set and a larger-scale CI method are employed in the calculations. Consequently, the calculated barrier height seems to lie in the range 80 ± 2 kcal mol⁻¹.

At present, a thermal rate constant for channel 1a is given only in the report of Just⁶ shown in Figure 9 as $k_{1a}(J)$, where $k_{1a}(J) = 10^{16.15} \exp(-71.5 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This is larger than k_1 by about 1 order of magnitude at 2000 K. It has been suggested that reaction 1a might be in the falloff region at the total density of $1 \times 10^{-5} \text{ mol cm}^{-3}$; however, except for the above report, there are no experimental data which suggest that k_{1a} is larger than k_1 . Like the present study, Dean et al.^{4,5} found that k_{1a} was not important under the conditions considered. Results of Batt et al.⁷ at lower temperatures from 750 to 850 K again showed no important role of channel 1a.

According to Forst's calculations²⁰ of falloff curves by considering the tunneling, the activation energy of k_{1a} decreased with decreasing total density, while that of k_1 did not change. This suggests a substantial lowering of k_1 relative to k_{1a} at very low total densities. Because all the experimental studies so far were limited to a narrow density region, it is necessary to investigate the reaction kinetics over an expanded density range.

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(24) JANAF Thermochemical Tables, Supplement *J. Phys. Chem. Ref. Data* 1974, 3, 311.

Radical Mechanism for the Laser-Induced Explosion of Methyl Isocyanide

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The laser-induced isomerization of methyl isocyanide has previously been shown to exhibit a marked pressure dependence; large-scale isomerization occurs when threshold conditions have been exceeded. Recent investigations of this large-scale isomerization have shown that the threshold is not due to a thermal mechanism as previously believed. In this work, the characteristics of the threshold are examined and it is shown that the threshold is a result of a radical channel.

I. Introduction

In recent years, there have been numerous investigations of laser-induced chemical reactions.^{1,2} Although it is well-known

that laser-induced reactions can occur under completely collisionless conditions,³⁻⁵ there have been a number of studies doc-

(1) Schulz, P. A.; Sudbo, A. S.; Krajnovich, D. J.; Kwok, H. S.; Shen, Y. R.; Lee, Y. T. *Annu. Rev. Phys. Chem.* 1979, 30, 379.

(2) Ronn, A. *Sci. Am.* 1979, 114.

(3) Coggiola, M. J.; Schulz, P. A.; Lee, Y. T.; Shen, Y. R. *Phys. Rev. Lett.* 1977, 38, 17.

TABLE I: Products from the Irradiation of Pure Methyl Isocyanide^a

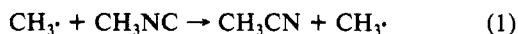
no. pulses	init press., ^b torr	products press., ^c torr						
		CH ₃ CN	CH ₃ NC	HCN	CH ₄	C ₂ H ₃ CN	C ₂ H ₄	C ₂ H ₂
1	13.00	10.51	0.17	0.59	0.21	trace	0.04	0.04
50	10.50	0.65	9.30				0.03	

^a Irradiation fluence is $2.76 \pm 5\%$ J/cm². With this fluence, the threshold pressure for pure methyl isocyanide is 12.7 ± 0.2 torr. ^b ± 0.01 torr. ^c ± 0.05 torr.

umenting a significant enhancement of both absorption and yield with increasing pressure.⁶⁻¹³ A dramatic example of increased yield with pressure is the isomerization of methyl isocyanide to acetonitrile. For this isomerization, there exists a sharp threshold pressure above which there is nearly complete isomerization of the material in the cell despite irradiation of a small fraction of the cell.¹⁴⁻¹⁶ Below this threshold pressure, the conversion per pulse is much less than 1%.

The threshold behavior of the methyl isocyanide isomerization has been observed previously^{14,15} and was attributed to a laser-initiated thermal explosion¹⁴ owing to the exothermicity of the reaction. However, recent theoretical and experimental work in our laboratory have shown¹⁶ and confirmed¹⁷ that this thermal-explosion model does not account for the experimental data. Therefore, we began to search for the trigger of the explosion.

The results of this search indicate that the threshold is a radical-chain-initiated explosion. A radical-chain component



has previously been suspected in the thermal isomerization of methyl isocyanide. In a series of papers, Pritchard et al. report both the observation of minor concentrations of methane and HCN (0.1–0.5% of the acetonitrile produced)¹⁸ and the isomerization of methyl isocyanide by methyl radicals.^{19,20} However, later results with radical scavengers added to the methyl isocyanide²¹ cast doubt on this interpretation, making the status of the radical channel ambiguous. In contrast, the laser-induced reaction enhances the radical channel and typically produces 4.5% HCN and 1.6% methane. Thus, the evidence for a radical channel is much stronger in the laser-initiated reaction. Further evidence for a radical-chain mechanism includes the appearance of a solid, nonvolatile material upon irradiation of samples of moderate pressure (>30 torr) as well as the appearance of significant concentrations of ethylene following irradiation of subthreshold samples.

The radical channel becomes more significant as the pressure and fluence are raised. This is demonstrated by examining the reaction products as a function of pressure and fluence. As the pressure increases, the yield of CH₄, HCN, and C₂H₄ per torr of sample increases and the relative concentration of unreacted methyl isocyanide decreases. As the fluence is lowered, the yield of CH₄ and HCN decreases and acetonitrile increases. To confirm the role of radicals in this reaction, a methyl radical source, di-*tert*-butyl peroxide (DTBP), was added to samples of methyl isocyanide. Receiving its energy from collisions with methyl isocyanide, DTBP lowered the threshold for the isomerization.

The experiments for the above-summarized results will be presented in section III and the results will be discussed in section IV.

II. Experimental Section

The essential details of the experimental setup have been described previously.^{16,17} For these experiments, the laser was operated on the P(20) line of the 10.6- μm transition. Nondestructive preirradiation sample analysis was performed with an IBM Instruments Model 85 FTIR. Postirradiation analysis was performed with the FTIR and three other instruments: a Hewlett-Packard 5750 gas chromatograph interfaced to an IBM Instruments CS9000 computer, a Hitachi-Perkin-Elmer Model RMU-6 mass spectrometer, and/or a Hewlett-Packard Model 5992-A GC-MS.

DTBP was obtained from Pfaltz and Bauer, degassed, and transferred on the vacuum line. It was then stored in an evacuated vessel.

III. Results

All four sets of experiments that were performed, product analysis, pressure dependence of the products, fluence dependence of the products, and addition of di-*tert*-butyl peroxide, contribute to the overall picture for the trigger of the explosive isomerization. Thus the experiments and the associated data will be presented first.

Product Analysis. Previous investigators²² have reported the observation of acetonitrile, C₂H₂, and HCN upon irradiation of methyl isocyanide. Additional products have been acknowledged²³ but not identified. In addition to acetonitrile as the major product, we also observed minor products of this reaction both directly as small peaks on the gas chromatograph and indirectly as the difference between the original methyl isocyanide pressure and the sum of the final methyl isocyanide and acetonitrile partial pressures. Since identification of the reaction products is important for understanding the reaction mechanism, a set of experiments was performed for identification purposes.

Samples are normally irradiated in a 1-in.-long, 1-in.-diameter cell to minimize the fluence variation along the cell axis. (Methyl isocyanide is a weak absorber, so this variation is <1.5% over the length of the cell.) However, since the pressure of the minor products is small, use of this cell made product identification difficult. Thus, samples were irradiated in a 7-in.-long, 1 1/2-in.-diameter cell. The products formed with this cell are the same as those with the smaller cell.

Following irradiation of a 36-torr sample in the larger cell, an FTIR spectrum of the products was obtained. This trace clearly shows a series of methane peaks at 3020 cm⁻¹, an acetylene peak

(4) Grant, E. R.; Coggiola, M. J.; Lee, Y. T.; Schulz, P. A.; Sudbo, Aa. S.; Shen, Y. R. *Chem. Phys. Lett.* **1977**, *52*, 595.

(5) Kolodner, P.; Winterfeld, C.; Yablonovitch, E. *Opt. Commun.* **1977**, *20*, 119.

(6) Lussier, F. M.; Steinfeld, J. I.; Deutsch, T. F. *Chem. Phys. Lett.* **1978**, *58*, 277.

(7) Quigley, C. P. *Opt. Lett.* **1978**, *3*, 106; *J. Photochem.* **1978**, *9*, 177.

(8) Peterson, N. C.; Manning, R. G.; Braun, W. *J. Natl. Bur. Stand.*, **1978**, *83*, 117.

(9) Quick, C. R., Jr.; Wittig, C. *Chem. Phys.* **1978**, *32*, 75; *J. Chem. Phys.* **1978**, *69*, 4201.

(10) Stephenson, J. C.; King, D. S.; Goodman, M. F.; Stone, J. *J. Chem. Phys.* **1979**, *70*, 4496.

(11) Herman, I. P.; Marling, J. B. *Chem. Phys. Lett.* **1979**, *64*, 75.

(12) Duperrex, R.; van den Bergh, H. *Chem. Phys.* **1979**, *40*, 275.

(13) Duperrex, R.; van den Bergh, H. *J. Chem. Phys.* **1979**, *71*, 3613.

(14) Bethune, D. S.; Lankard, J. R.; Loy, M. M. T.; Ors, J.; Sorokin, P. *Chem. Phys. Lett.* **1978**, *57*, 479.

(15) Hartford, A.; Tuccio, S. *Chem. Phys. Lett.* **1979**, *60*, 431.

(16) Shultz, M. J.; Rock, E. J.; Tricca, R. E.; Yam, L. M. *J. Phys. Chem.* **1984**, *88*, 5157.

(17) Shultz, M. J.; Tricca, R. E.; Yam, L. M. *J. Phys. Chem.* **1985**, *89*, 58.

(18) Shaw, D. H.; Pritchard, H. O. *J. Phys. Chem.* **1966**, *20*, 1230.

(19) Yip, C. K.; Pritchard, H. O. *Can. J. Chem.* **1970**, *48*, 2942.

(20) Shaw, D. H.; Dunning, B. K.; Pritchard, H. O. *Can. J. Chem.*, **1969**, *47*, 669.

(21) Collister, J. L.; Pritchard, H. O. *Can. J. Chem.* **1976**, *54*, 5380.

(22) Hicks, K. W.; Lesiecki, M. L.; Riseman, S. M.; Guillory, W. A. *J. Phys. Chem.* **1979**, *83*, 1936.

(23) Kleinermanns, C.; Wagner, H. G. *Ber. Bunsenges. Phys. Chem.* **1977**, *81*, 1283.

TABLE II: Products from the Irradiation of Mixtures of Methyl Isocyanide and Di-*tert*-butyl Peroxide^a

no. pulses	reactant press., ^b torr		products press., ^b torr							
	CH ₃ CN	DTBP	CH ₃ CN	CH ₃ NC	HCN	CH ₄	C ₂ H ₅ CN	C ₂ H ₆	C ₂ H ₂	(CH ₃) ₂ CO
1	12.72	0.78	9.65	2.02	1.13	0.93	0.44	0.55	0.06	0.45
1	11.58	0.72	8.75	2.01	0.91	0.75	0.41	0.52	0.05	0.47
1	10.94	0.72	8.25	2.03	0.98	0.70	0.41	0.51	trace	0.52
50	10.68	0.74	0.67	9.49		0.02		0.61		1.09

^a Irradiation fluence is $2.76 \pm 5\%$ J/cm². With this fluence, the threshold pressure for pure methyl isocyanide is 12.7 ± 0.2 torr. ^b ± 0.10 torr.

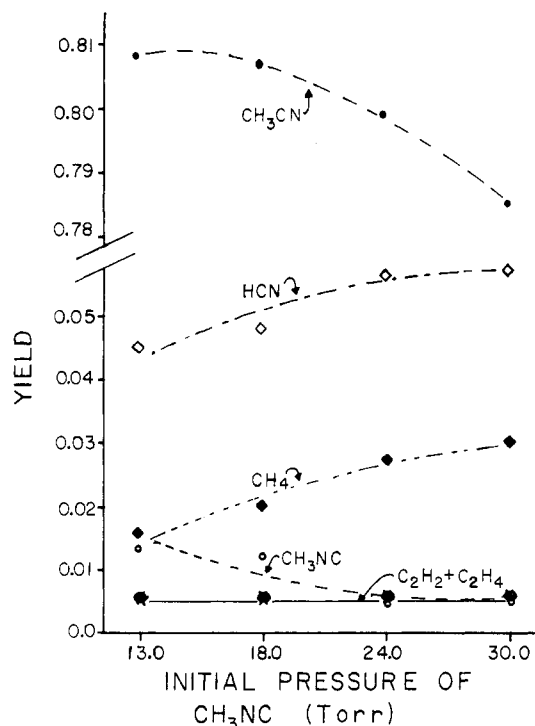


Figure 1. Pressure dependence of the products of the laser-induced isomerization of methyl isocyanide for the range 13.0–30.0 torr. The yield is the ratio of the partial pressure of the product to the initial pressure of methyl isocyanide. Irradiation fluence is $2.76 \pm 5\%$ J/cm². With this fluence, the threshold pressure for pure methyl isocyanide is 12.7 ± 0.2 torr.

at 729 cm^{-1} , and an HCN peak at 713 cm^{-1} , in addition to the acetonitrile spectrum. Since the remaining products are present in even smaller concentrations, the products were subjected to mass spectral analysis which indicated the presence of ethylene and propionitrile. Subsequent GC-MS analysis confirmed the above and also indicated the presence of propylene.

After identification, quantitative analysis of the products was performed with the gas chromatograph. Results from a typical 13-torr sample are shown in Table I. Notice that CH₄ and HCN are the most abundant of the minor products. These are followed by ethylene and acetylene and, in even smaller concentration, propionitrile.

The remaining product of the reaction is observable when the pressure in the cell exceeds 30 torr. Upon irradiation of a sample of 30 torr or greater, a white cloud is observed spreading out from the irradiated zone to the cell walls. This cloud is a nonvolatile product that accounts for an increasingly large portion of the methyl isocyanide consumed as the initial sample pressure is increased.

In order to determine if the minor products are present below threshold, a subthreshold sample (10.5 torr) was irradiated. The results of this experiment are shown in Table I, which indicates a significant concentration of ethylene in addition to the acetonitrile produced. A subsequent sample was irradiated for 3 h at 0.07 Hz and HCN was also observed.

A similar product analysis for the isomerization of ethyl isocyanide to ethyl cyanide reveals the minor products to be mainly C₂H₄, HCN, and C₂H₆ with smaller concentrations of CH₄ and C₃H₆. In addition, there is a nonvolatile product similar to that

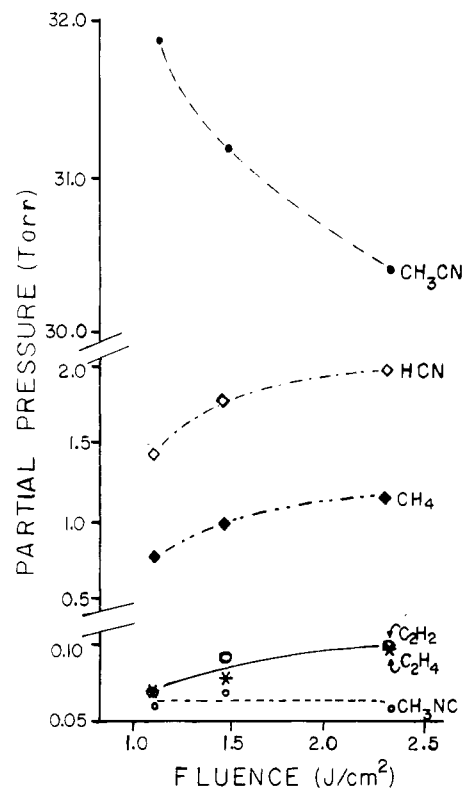


Figure 2. Fluence dependence of the products of the laser-induced isomerization of methyl isocyanide for the range $1.10\text{--}2.33 \pm 0.5\%$ J/cm². Sample pressure was 36 torr.

observed in the methyl isocyanide reaction.

Pressure Dependence of the Products. To determine the effect of increasing pressure on the reaction, the pressure was varied from 13.0 to 30.0 torr while keeping the incident fluence constant at $2.76 \pm 5\%$ J/cm². With this incident fluence, the explosion threshold is 12.7 ± 0.2 torr. For these experiments, the 1-in.-diameter, 1-in.-long cell was used to minimize the fluence variation along the cell axis.

The results of this set of experiments are shown in Figure 1, which displays the product yield per torr of methyl isocyanide reactant as a function of the initial pressure. Notice that both the acetonitrile yield per torr and the amount of unreacted methyl isocyanide fall as a function of pressure, while the yield of HCN and methane rises.

Fluence Dependence of the Products. To determine the effect of decreasing fluence on the reaction, the 1-in.-long, 1-in.-diameter cell was filled to 36 torr and irradiated with a single pulse. In this set of experiments, the fluence was varied from a high of $2.33 \pm 5\%$ J/cm² to a low of $1.10 \pm 5\%$ J/cm² by attenuation with CaF₂ flats.

The results of this experiment are presented in Figure 2 which shows the partial pressure of the products as a function of the incident fluence. Notice that the production of acetonitrile increases, while the yield of HCN and methane decreases as the fluence is lowered. The amount of unreacted methyl isocyanide is very small and virtually constant.

Addition of Di-*tert*-butyl Peroxide. In order to generate methyl radicals in the system, 0.7 torr of DTBP was added to slightly subthreshold-pressure samples of methyl isocyanide in the 1-

in.-diameter, 1-in.-long cell. The results of this experiment are given in Table II. Notice that the products of the sample containing DTBP include acetone and ethane which are a direct result of the decomposition of the DTBP. Aside from acetone and ethane, the products of the DTBP/methyl isocyanide mix are the same as those from a pure methyl isocyanide sample. However, the yields of methane, HCN, and propionitrile are greater in the mix than in the pure methyl isocyanide.

IV. Discussion

The above results are consistent with the conclusion that the explosion threshold in the laser-induced isomerization of methyl isocyanide is a result of a radical-reaction channel. In the sub-threshold region, this channel probably competes with the thermal, unimolecular channel. However, as the pressure or fluence is raised, the radical channel becomes increasingly important, ultimately producing the explosion. The results of other investigators are consistent with this interpretation.

Product Analysis. The first indication that radicals are involved in the explosion was obtained from a product analysis. The results of this analysis, listed in Table I, indicate 1.6% conversion to methane and 4.5% conversion to HCN. It is instructive to compare this with the direct dissociation of methyl isocyanide with a focused beam. The products of the direct dissociation include HCN and acetylene,²² while both methane and acetylene are observed in the present experiments with methane always present in larger concentrations. To produce the direct dissociation, the fluence in the above-cited experiments was 111 J/cm², nearly 2 orders of magnitude higher than those under consideration here. This higher fluence not only enhances the direct dissociation, but also results in more energetic intermediates so the production of two-carbon hydrocarbons is favored over that of methane.

In contrast, the methyl radicals generated in the present experiments find their fate through several channels, including hydrogen abstraction to produce methane. Note that hydrogen abstraction by methyl radicals from methyl cyanide to produce methane has been documented by Wijnen²⁴ and found to have a 10.0 ± 0.5 kcal/mol activation barrier. Assuming the activation barrier for hydrogen abstraction from methyl isocyanide to be comparable, this reaction would readily compete with the radical-chain propagation step (eq 1).

It is the appearance of significant quantities of methane under the milder conditions of the present experiments that begins to indicate the importance of methyl radicals in *triggering* the explosion. The question that remains is whether methyl radicals initiate a chain and trigger the explosion, or whether the smaller products results from an explosion triggered by another source. The DTBP experiments, discussed below, support the conclusion that the radicals trigger the explosion.

Addition of Di-tert-butyl Peroxide. Conclusive evidence for the role of methyl radicals in the initiation of the explosion comes from experiments with DTBP added to methyl isocyanide. In these experiments, 0.7 torr of DTBP was added to samples as much as 1.5 torr below the threshold for pure methyl isocyanide. Upon irradiation with $2.76 \pm 5\%$ J/cm², these samples exploded.

To determine whether the explosion was merely due to an increase in the total pressure in the cell, several other gases were added to methyl isocyanide. These include Ar, CO₂, ethane, propylene, ethyl isocyanide, acetonitrile, and propionitrile. These gases represent a large range of heat capacities, vibrational degrees of freedom, and reactivity. All addends were found to *raise* the explosion threshold.²⁵ Thus, DTBP *lowers* the threshold due to its propensity for production of methyl radicals.

Table II lists the products from DTBP/methyl isocyanide mixtures, and Figure 3 compares them to those from the pure methyl isocyanide explosion. The products, acetone and ethane, are a direct result of dissociation of DTBP. DTBP itself absorbs less than 0.2% at 944.19 cm⁻¹ and no reaction occurs when pure DTBP is irradiated at this wavelength. Therefore, reaction of the

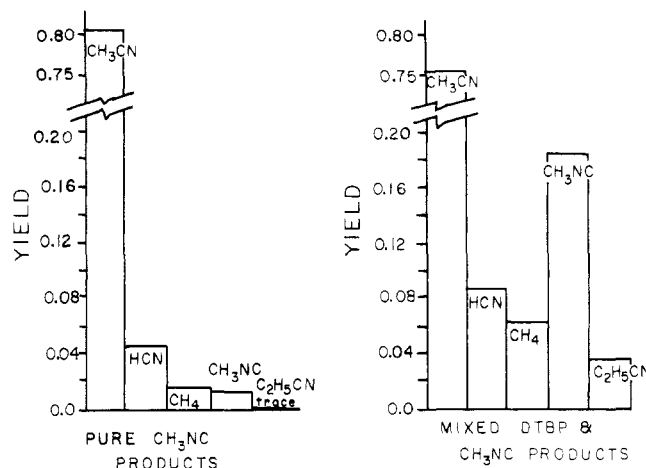
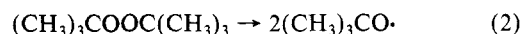


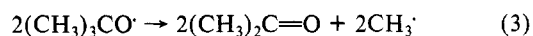
Figure 3. Comparison of the products of the explosive isomerization of methyl isocyanide for samples of pure methyl isocyanide and samples of mixed methyl isocyanide and di-tert-butyl peroxide. The yield is the ratio of the partial pressure of the product to the initial pressure of methyl isocyanide.

DTBP must result from the collisional transfer of energy initially deposited in the methyl isocyanide. Results also show that the partial pressure of the methane is significantly increased, confirming that one channel for the methyl radicals is hydrogen abstraction to produce methane.

Having shown that methyl radicals both lower the threshold and enhance the production of methane, it is informative to discuss the energetics of this mixture. The activation barrier for the reaction



is 39.1 ± 0.5 kcal/mol,²⁶ an energy very comparable to the 38.8 kcal/mol activation energy for the methyl isocyanide isomerization.²⁷ The net energy for the DTBP reaction, however, is very different from the methyl isocyanide isomerization. For (2) above, the reaction is known to continue as



which is endothermic by 43.5 kcal. This is followed by



The net reaction is exothermic by 44.7 kcal/mol,²⁸ while isomerization of methyl isocyanide is *exothermic* by 23.7 kcal/mol.²⁹ However, the heat capacity of the DTBP, which is originally at room temperature, is much larger than that of either methyl isocyanide or acetonitrile. Thus, DTBP acts as an energy sink and should quench the reaction. Although the increased concentration of unreacted methyl isocyanide in the mix and the corresponding decrease in the acetonitrile produced are a direct result of the DTBP acting as an energy sink, DTBP in fact lowers the threshold. Hence, the methyl radicals produced in (3) must propagate a chain reaction which results in nearly complete isomerization of the methyl isocyanide.

The above evidence implies that the direct dissociation channel is less important in the DTBP-produced explosion than in the pure methyl isocyanide explosion. Hence, the increased methane and HCN concentrations must be due to the enhanced radical channel. The appearance of methane in small concentrations in the sub-threshold sample with DTBP added (Table II) confirms the conclusion that methane is produced from methyl radicals.

Pressure Dependence. Since the sample pressure is a critical parameter, the pressure effects were examined. The results for the range 13.0–30.0 torr are shown in Figure 1 which indicates the yield per torr as a function of the pressure. Notice that as the pressure is raised, the relative production of acetonitrile and

(24) Wijnen, M. H. J. *J. Chem. Phys.* **1954**, *22*, 1074.

(25) Shultz, M. J.; Tricca, Robert E., in preparation.

(26) Raley, J. et. al. *J. Am. Chem. Soc.* **1948**, *70*, 88.

(27) Schneider, F. W.; Rabinovitch, B. S. *J. Am. Chem. Soc.* **1962**, *84*, 4215.

the relative amount of unreacted methyl isocyanide decrease. Although it is tempting to attribute this difference to an increased production of HCN, this increase is not sufficient. The sum of the pressures of all measured nitrogen-bearing compounds is significantly less than the original pressure of methyl isocyanide. Since there is no methyl isocyanide pressure loss for nonirradiated samples after several hours, this pressure discrepancy must be due to formation of a nonvolatile material. The yield per torr of this material increases as the initial sample pressure is raised. Formation of this material is further evidence that radicals are indeed involved in this reaction.

Fluence Dependence. Increasing the pressure reduces the mean free path, and thus increases the production of methane, HCN, and the nonvolatile material. These are the same effects that one would observe as the energy density in the sample is raised since increased fluence produces materials with a higher energy content. In a series of experiments, the fluence effects on the yield were examined and the results are given in Figure 2. These show that as the energy density incident on the sample is raised from $1.10 \pm 5\%$ to $2.33 \pm 5\%$ J/cm², the production of methane, HCN, and the nonvolatile material is increased.

This experiment gives additional support for the methyl-radical channel, since it is known that methyl radical-radical recombination yields increasingly unsaturated two-carbon hydrocarbons as the energy is increased. Consistent with the interpretation of increasingly energetic methyl radicals, the results of this experiment show that as the energy density is raised, the production of ethylene and acetylene increases.

Other Evidence. Results from the laser-induced isomerization of ethyl isocyanide³⁰ are consistent with the conclusion that the explosion is radical initiated. The threshold pressure in ethyl isocyanide is much lower than the threshold in methyl isocyanide for similar irradiation conditions. For example, with $2.76 \pm 0.5\%$ J/cm² incident and comparable energy absorbed, the threshold pressure in ethyl isocyanide is 5.0 ± 0.3 torr while that for methyl isocyanide is 12.7 ± 0.2 torr. This lower threshold is a consequence of the greater stability of the ethyl radical, resulting not only in a more facile formation but also in a longer lifetime. Hence, both the mean-free path and the energy requirements are lower for the ethyl isocyanide. Observation of ethane in the ethyl isocyanide isomerization is further evidence for the importance of ethyl radicals in this isomerization.

Several investigators^{18-20,31,32} have suggested the importance of a radical channel in the isomerization of methyl isocyanide. Condensed-phase experiments using optically active compounds^{31,32} have reported a loss of optical activity, sometimes as large as 13%,

on isomerization. As mentioned in the introduction, evidence for a radical channel in the gas-phase thermal isomerization is more ambiguous.

The initiation step for the radical chain is still in doubt. Two possibilities are direct bond fission and α -hydrogen abstraction followed by elimination of HCN. Of these, direct bond fission has the advantage of simplicity. However, laser-initiated bond fissions generally require average excitations of 20 or more photons, much greater than the 1-4 photons of the current experiments.¹⁷ Indeed, previous investigations of bond fission in methyl isocyanide^{22,33} have utilized focused beams to attain such high energy densities. In addition, comparison of the temporal behavior of the CN^{*} emission with the emission from the pyrolysis of acetonitrile³³ suggests that CN^{*} is a result of the explosion rather than the cause of it. When a subthreshold sample of methyl isocyanide was irradiated for several hours at 0.07 Hz, the products included acetonitrile, ethylene, and a very small concentration of HCN. This observation strengthens the conjecture that the initial radical production is a consequence of a bimolecular process. Further experiments are under way to evaluate this possibility.

V. Summary

We have examined the laser-induced explosion of methyl isocyanide to acetonitrile in order to determine the initiation step. By coupling a thorough product analysis with pressure and fluence studies, it appears that this reaction has two concurrent channels: a thermal, unimolecular channel and a radical-chain channel. As either the sample pressure or the incident energy density is increased, the radical channel becomes increasingly important. Finally, when the pressure-fluence combination reaches a critical value, the radical chain propagates the reaction throughout the cell. (The equation relating the pressure and fluence to give the critical value is given in ref 17.)

Addition of a small amount of a methyl radical source, DTBP, confirms the interpretation that the threshold is due to a radical mechanism. Analysis of the present data along with earlier studies of the isomerization of isocyanides suggests that the initiation step for the radical mechanism in pure methyl isocyanide samples is due to an α -hydrogen abstraction followed by elimination of HCN. Further experiments to evaluate this possibility are currently under way.

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Registry No. CH₃NC, 593-75-9; di-*tert*-butyl peroxide, 110-05-4.

(28) Calculated from: "CRC Handbook", 62nd ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1981. Baker et. al. *J. Chem. Soc.* **1965**, 6970. Herschel, *J. Phys. Chem.* **1941**, *45*, 1316.

(29) Baghal-Vayjooee, M. *Can. J. Chem.* **1977**, *55*, 2634.

(30) Shultz, M. J.; Yam, L. M.; Berets, S. L.; Rock, E. J., in preparation.

(31) Casanova, J., Jr.; Werner, N. D.; Schuster, R. E. *J. Org. Chem.* **1966**, *31*, 3473.

(32) Yamada, S.; Takashima, K.; Sato, T.; Terashima, S. *Chem. Commun.* **1969**, 811.

(33) Bethune, D. S.; Lankard, J. R.; Loy, M. M. T.; Ors, J.; Sorokin, P. P. "Laser-Induced Processes in Molecules"; Springer-Verlag: West Berlin, 1979; Springer Ser. Chem. Phys., Vol. 6, pp 193, 194.