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TECHNICAL REPORT RD-RE-88-6

SELECTIVE NITRATIONS: LASER-INDUCED NITRATIONS

A. E. Stanley and S. E. Godbey
Research Directorate
Research, Development, and Engineering Center

JANUARY 1989



U.S. ARMY MISSILE COMMAND

Redstone Arsenal, Alabama 35898-5000

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*A National Research Council (NRC) Research Associate.

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| 19. ABSTRACT (Continue on reverse if necessary and identify by block number) The Army uses nitrated compounds as explosives and propellants. There is a special need for propellants with the chemical composition necessary to burn exactly with a minimum of side products which create smoke, but with high energy production. An important part of this process is the ability to selectively nitrate materials. Laser-induced chemistry possesses the potential to drive some reactions in an efficient and selective manner. Laser-induced chemistry may be useful in driving nitration reactions toward specific products. Reported herein are the results of several successful attempts to laser-induce the reaction of nitrogen dioxide with hydrocarbons of 3, 4 and 5 carbons. Specifically, the tunable continuous wave infrared laser was used to drive the reaction between nitrogen dioxide, and propane, n-butane, isobutane, and n-pentane. The major products of the reactions were secondary (tertiary in the isobutane reaction) nitrohydrocarbons, of the same chain length as the reacting hydrocarbon. Some short chain nitrated compounds were also identified. The yield of 2-nitrobutane observed in the nitration of butane is approximately 20% based on the depletion | | | | | |
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of nitrogen dioxide. The propane reacted with nitrogen dioxide to produce mostly 2-nitropropane with a smaller yield of 5-9%. The analogous reaction of pentane produced approximately 9% of the major product which is believed to be 2-nitropentane. The isobutane nitration resulted in approximately a 10% yield of 2-methyl-2-nitropropane. The results of these laser-induced reactions are contrasted to the corresponding thermal reactions. The reaction mechanism is also discussed for these two processes.

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Appreciation is extended to Dr. V. F. Kalasinsky of Mississippi State University for providing the samples of isobutane and t-butyl nitrite. We would also like to acknowledge the Chemistry Department of the University of Alabama in Huntsville, for assistance in recording the NMR spectrum of 2-nitrobutane.



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I. INTRODUCTION

Most of the nitrated compounds used by the Army are explosives and propellants. Current nitration methods often result in low yields of desired products and complex mixtures of reaction products. Laser-induced chemistry shows the promise of being an efficient and selective procedure. In this study, it is intended to use a continuous wave (CW), carbon dioxide (CO₂) laser to drive the nitration of several hydrocarbons (C₃, C₄, and C₅) by nitrogen dioxide (NO₂).

Traditionally, nitration of paraffins is difficult to accomplish. High temperature (200 - 400 °C) and high pressure (8-12 atmospheres) reactors are used with some success in the commercial production of nitroalkanes [1]. However, new methods are continually sought which will increase the currently low yields of nitroparaffins and minimize the troublesome side reactions. Efficient control over which nitroalkanes are produced (selective nitration) in these processes is also desirable.

Recently, Umstead, et al. reported the photonitration of isobutane by nitrogen dioxide (NO₂) using an argon-ion laser as the excitation source [2,3]. The NO₂ absorbs the radiation and then, according to the kinetic modeling [3], the vibronically excited NO₂ (NO₂*_v) achieves the direct abstraction of a hydrogen atom from the isobutane. The resulting free radical reacts primarily with NO₂ to form 2-methyl-2-nitropropane. However, the yield of 2-methyl-2-nitropropane based on isobutane was low (about 2.6 percent) and product fragmentation was reported to be significant.

II. EXPERIMENTAL

Samples of propane, n-butane, n-pentane, nitromethane, nitroethane, 1-nitropropane, 2-nitropropane, 2-methyl-2-nitropropane, 1-nitrobutane, 1-nitropentane, and nitrogen dioxide were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin. The samples were of 98 percent or greater stated purity except for 2-nitropropane which was 94 percent stated purity. The isobutane and t-butyl nitrite samples were provided by V. F. Kalasinsky. The purity of the samples was monitored using gas chromatography-mass spectroscopy (GC-MS) and the infrared spectra were compared to published spectra where literature spectra were available [4-10]. No further purification of these compounds was undertaken with the exception of nitrogen dioxide which was purified by trap-to-trap separation at -78.5 °C. All compounds were degassed at -196.8 °C.

A stainless steel cell of exterior dimensions 5x5x10 cm was used to hold reactants during irradiation. This cell was equipped with zinc selenide windows on the long path through which the laser was directed and KRS-5 or KCl windows on the short path for collecting the infrared spectra of reactions and products. The optical pathlength of the long path was 10.5 cm while the short optical pathlength was 5 cm.

The infrared spectra were recorded on a Bomem DA3.002 interferometer equipped with a vacuum bench and having a deuterated TGS detector and a KBr beamsplitter. The effective resolution was 1 cm^{-1} and 32 scans were taken for each sample and reference. A medium apodization function [11] was used.

The initial sample pressures were measured using an MKS Baratron electronic manometer, consisting of a type 222B transducer and a type PDR-5B digital readout power supply.

A Coherent Radiation model 41 CW, CO_2 tunable laser provided the energy to drive the reactions, and was operated in a single mode at various selected wavelengths and powers. The wavelength was verified using an Optical Engineering CO_2 spectrum analyzer. The powers were measured by a Coherent Radiation model 213 water-cooled power meter.

The reaction cell was positioned on a movable stage which could be translated along the laser path. All samples were irradiated with the cell positioned behind the focal point where the beam was slightly diverging. The zinc selenide window allowed a beam transmittance of about 70 percent through to the sample. The reported powers of laser fluences do not correct for this window absorption nor the difference in beam diameter at the sample versus at the power meter where the beam is larger. The beam diameter was approximately 2 mm at the point of entry to the reaction cell.

The separation and analysis of reaction product were accomplished partly by using a Hewlett Packard (HP) 5890 gas chromatograph equipped with a gas sampling loop and interfaced to a HP 5970 series mass selective detector. The chromatographic column identified was an HP Ultra 2 (crosslinked 5 percent phenyl methyl silicone) of about 40 m length having 0.2 mm interior diameter and 0.33 micrometer film thickness. The volumetric flow rate was $\sim 1.6\text{ cm}^3/\text{min}$ (linear flow rate $\sim 10\text{ m}/\text{min}$); the split ratio was $\sim 47:1$ and the column head pressure was 10 psi. The instrument response to each commercially available nitroparaffin was estimated by filling the reaction cell with known pressures of the pure compounds and sampling into the gas sampling loop. The responses versus initial pressure of the components were plotted to give a calibration curve for each component. The nitroalkanes which were not available to use as standards, namely 2-nitrobutane, 1-nitro-2-methylpropane, 2-nitropentane, and 3-nitropentane, were treated as having approximately the same instrument response as 1-nitrobutane. The separation of some highly volatile components was not possible with the chromatographic conditions used.

III. RESULTS

The intent of this project was to laser-induce the reactions of nitrogen dioxide or nitric acid with hydrocarbons of 3, 4 or 5 carbons. The laser used in this initial study was a carbon dioxide infrared laser which can be set on a frequency resonant with a vibrational frequency of the hydrocarbon reactant. A sensitizer such as sulfur hexafluoride can be used if necessary to drive the reaction. With special attention to details such as the absorption spectra of the nitration products, our expectation was to select excitation conditions which increase the yield of specific desired products and minimize product decomposition.

A. Propane/NO₂

The infrared spectrum of propane in the 1100-900 cm⁻¹ region (Fig. 1A) revealed two vibrational bands that are accessible by the output of the CO₂ laser. Of these, the one centered at 923 cm⁻¹ is slightly stronger and was chosen for use in this initial study. Two regions on this band seemed particularly suited for irradiation by a CO₂ laser. The first is in the region of the Q branch which is a good match to the P(40) line of the (00¹-10⁰) transition at 925 cm⁻¹ [12]. The other is the P(30) component of this same CO₂ laser band at 935 cm⁻¹ which corresponds approximately to the maximum point on the R branch of the propane spectrum. Higher laser powers were possible with the P(30) line but the higher relative absorptivity of the propane Q branch to the R branch makes the P(40) line the better choice. The nitration of propane was difficult using either line. However, utilizing the P(40) line at a power of 82 W/cm², the nitration of propane was more successful. A propane pressure of 470 torr and an irradiation time of 60 sec resulted in the conversion of ~ 15 percent of the NO₂, an initial pressure, 30 torr, to nitroparaffins. The yield of the major product, 2-nitropropane, was about 5 percent (see Table 1). The nitrated products, 2-nitropropane, 1-nitropropane, nitromethane, and nitroethane, were readily identified by comparison of their retention times and mass spectra to those of known compounds. However, the more volatile reaction products were not well separated in the gas chromatograms. The infrared spectrum of products as shown in Figure 2 and tabulated in Table 1, allowed identification of NO, CO₂, CO, and H₂O [13]. The region of the infrared spectrum of reactants and products used to identify NO, CO, and CO₂ can be seen in Figure 3.A(2). A higher pressure of propane (550 torr with remaining conditions the same as above) resulted in a higher yield of nitrated products (~ 22 percent) and a higher yield of the primary product, 2-nitropropane (~ 9 percent). The chromatogram of this product mixture is shown in Figure 4A and summarized in Table 2. Irradiation at the P(30) frequency resulted in lower yields of nitrated products, even at higher laser powers up to 100 W/cm², the highest power attempted for this compound.

B. n-Butane/NO₂

The overlapping bands near 960 cm⁻¹ in the infrared spectrum of butane (Figure 1B) are accessible by the output of the CO₂ laser. The P(6) line [12] of the (00¹-10⁰) at 956.1857 cm⁻¹ was chosen for this experiment since it coincides with the Q branch near 956 cm⁻¹ in the butane spectrum. About 40 percent of the NO₂ was converted to nitroparaffins when a mixture of 220 torr butane and 20 torr NO₂ was irradiated for 30 sec with 75 W/cm² laser power. Approximately half of the total nitroparaffin yield arises from one component which is thought to be 2-nitrobutane based upon its mass spectrum and its retention time, 11.49 min (Fig. 4 and Table 3). This is longer than the retention time of 1-nitropropane (10.10 min) and shorter than the 1-nitrobutane retention time (12.930 min). We were unable to obtain 2-nitrobutane commercially to confirm the identify of this component. However, we were able to synthesize 2-nitrobutane from the oxidation of 2-aminobutane. The major product of this oxidation was identical in retention time and mass spectrum to the major product of the laser-induced nitration of butane. The proton nuclear magnetic resonance (NMR) spectrum of the product of the amine oxidation confirmed its identity as 2-nitrobutane. The remaining nitrated paraffins produced are nitroethane, nitromethane, 1-nitrobutane, and 1-nitropropane, in order of abundance. 2-nitropropane was not detected in the

nitration products. More nitroethane was produced than nitromethane. This is the reverse of what was found in the propane reaction. The products identified from the infrared, (Fig. 3B and 5 and Table 4) were NO, CO, CO₂ and H₂O. More CO seems to be present in the butane reaction products relative to the propane products.

C. n-Pentane/NO₂

The choice of a frequency for use in the laser-induced reaction of n-pentane with NO₂ was a compromise between the absorptivity of the bands in the infrared spectrum of n-pentane and the output power obtainable from the CO₂ laser in this region. The P(40) line of the (00¹-10⁰) transition of the CO₂ laser was satisfactory for our purpose. The laser-induced nitration of n-pentane was accomplished under conditions comparable to the butane experiments, that is, 220 torr pentane, 20 torr NO₂, 75 W/cm² laser power, and 30 sec irradiation time. A rough estimate of the total yield of nitrated paraffins is ~ 23 percent and of the major nitrated product ~ 9 percent. The primary product is probably 2-nitropentane, with about half as much 3-nitropentane being formed. This is a reasonable result, as both are secondary nitroparaffins and would be expected to be about equally favored as products. However, there are two equivalent positions on the n-pentane molecule which can be nitrated to yield 2-nitropentane, but only one which yields 3-nitropentane. The remaining nitroalkanes identified in the reaction products were, in order of abundance, nitroethane, 1-nitropropane, and 1-nitropentane. An impurity present in the pentane sample, cyclopentane, obscures the chromatographic peak of nitromethane (Fig. 4 and results tabulated in Table 5). It is likely that some of this compound was formed as well. It is again, as in the butane results, interesting to note the absence of particular nitrated products. No 2-nitropropane, 1-nitrobutane, or 2-nitrobutane were detected. The infrared spectrum, (Fig. 3C and 6, with results tabulated in Table 6), was again useful for identifying NO, CO, CO₂, and H₂O in the product mixture. The amount of CO present in the product mixture seems to be less in pentane, than in butane, (Fig. 3).

D. Isobutane/NO₂

The P(40) line of the (00¹-10⁰) band of the CO₂ laser was chosen for the isobutane/NO₂ irradiation. The frequency of this transition (924.9749 cm⁻¹) corresponds to a point on the only band of the isobutane molecule which is reasonably accessible to the output of the CO₂ laser. The laser-induced nitration of isobutane was accomplished under the following conditions: isobutane pressure, 350 torr; NO₂ pressure, 25 torr; laser power, 100 W/cm²; and irradiation time, 60 sec. The major nitroalkane produced was 2-methyl-2-nitropropane, with a yield of 10 percent estimated for this component. The total yield of nitroalkanes was approximately 23 percent (see Table 7). Nitromethane and 2-nitropropane have also been identified from the reaction products. Also, another nitroalkane having four carbons is produced and elutes after 2-methyl-2-nitropropane. The retention time and mass spectrum of this component are close to the same as the product identified in the butane nitration as 2-nitrobutane. However, it is unlikely that this is the product since rearrangement from a branched chain to a straight chain hydrocarbon is not expected. The mass spectra of nitrobutanes and nitromethylpropanes are very similar. Also, it is possible that the retention

times of 2-nitrobutane and 1-nitro-2-methylpropane are approximately the same under the chromatographic conditions utilized. For the present this product can only be questionably identified as 1-nitro-2-methylpropane.

Also identified in the GC-MS analysis of products were significant amounts of acetone and 2-methylpropane, and a smaller amount of 1-propene. The infrared spectrum (Fig. 7 and Table 8) of the products allowed identification of CO, CO₂, NO, and H₂O as well.

The pressure of the acetone in the product mixture prompted an interest in the decomposition of t-butyl nitrite as the likely precursor of this product. The laser-induced decomposition of t-butyl nitrite was accomplished using isobutane as the sensitizer to absorb the CO₂ laser output and transfer the energy to the t-butyl nitrite. The conditions employed were: isobutane pressure, 300 torr; t-butyl nitrite, 11 torr; laser line, P(40) of (00¹)-(10⁰) band; laser power, 100 W/cm²; irradiation time, 60 sec. The products which have been identified include acetone, 2-methylpropene, methane, 1-propene, and NO (see Figure 8 and Tables 9 and 10).

IV. CONCLUSION:

The CO₂ infrared laser-induced nitrations of propane, n-butane, isobutane, and n-pentane with NO₂ were successful. The products were found to be primarily secondary or tertiary nitroalkanes of the same chain length with smaller amounts of primary nitroalkanes and shorter chain nitroalkanes. The thermally-induced reaction between alkanes and NO₂ is described as proceeding via a free radical mechanism [1]. This should hold true when the excitation is provided by a laser. The primary reaction steps are thought to be



and



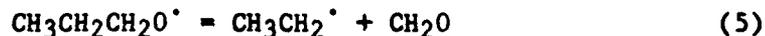
in the thermally-induced nitration of hydrocarbons, RH, using NO₂. An important side reaction is

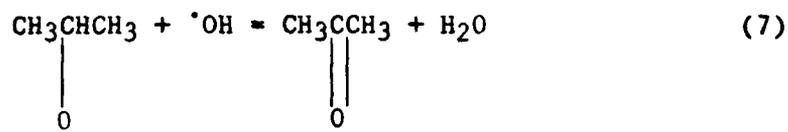
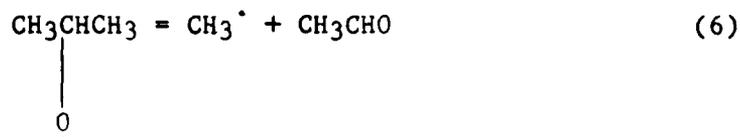


in which an unstable alkyl nitrite, RONO, is formed. The alkyl nitrite decomposes as follows:



although at conditions usually employed for nitrating hydrocarbons with NO₂, some of the alkyl nitrite might not decompose. The alkoxy radical, RO[·], produced in reaction (4), may undergo any of a number of reactions, including the following, using propyl radicals as examples:





The continued oxidation of aldehydes, ketones, alcohols, etc. produces acids, oxides of carbons, water, etc. The alkyl radicals formed in reactions (5), (6), and (8) could react with NO_2 to form lower molecular weight nitroalkanes. Alkyl radicals can also decompose directly to form lower molecular weight alkyl radicals which could react with NO_2 to form shorter chain nitroalkanes [21].

The specific products formed in the laser-induced nitrations are consistent with those reported from thermal nitrations [22]. For a comparison, see Table 11. Differences in conditions, such as the temperatures, pressures, ratio of hydrocarbon to nitrating agent, and nitrating reagent, (HNO_3 , in the thermal nitrations used for comparison), make quantitative comparisons unreliable. Further, a large experimental uncertainty is associated with our results, whenever known compounds are not available. Despite these drawbacks, the relative amounts of nitroalkanes produced in the propane irradiation fall within the range produced in the thermal nitrations at 505-10 °C and 790-5 °C. The butane results are close to the results from thermal studies as well. The pentane shows some differences. No 1-nitrobutane was detected in our product mixture, whereas the thermal reaction reported that 12.8 mole percent 1-nitrobutane was produced. The laser-induced nitration yielded about twice as much 2-nitropentane as 3-nitropentane. It is difficult to understand how 3-nitropentane could be produced at higher yields in the thermal reaction than 2-nitropentane. Both positions must arise from secondary alkyl radicals which should be roughly equivalent in stability. However, there are two equivalent positions on pentane which can yield 2-nitropentane, a fact which cannot be overcome by changing conditions. The results from the laser-induced reactions are very similar to the thermal results. The yields of nitrated products are promising. Further work is planned to optimize conditions and improve these results. The kinetics of these systems is of interest and plans are underway for modeling the reactions.

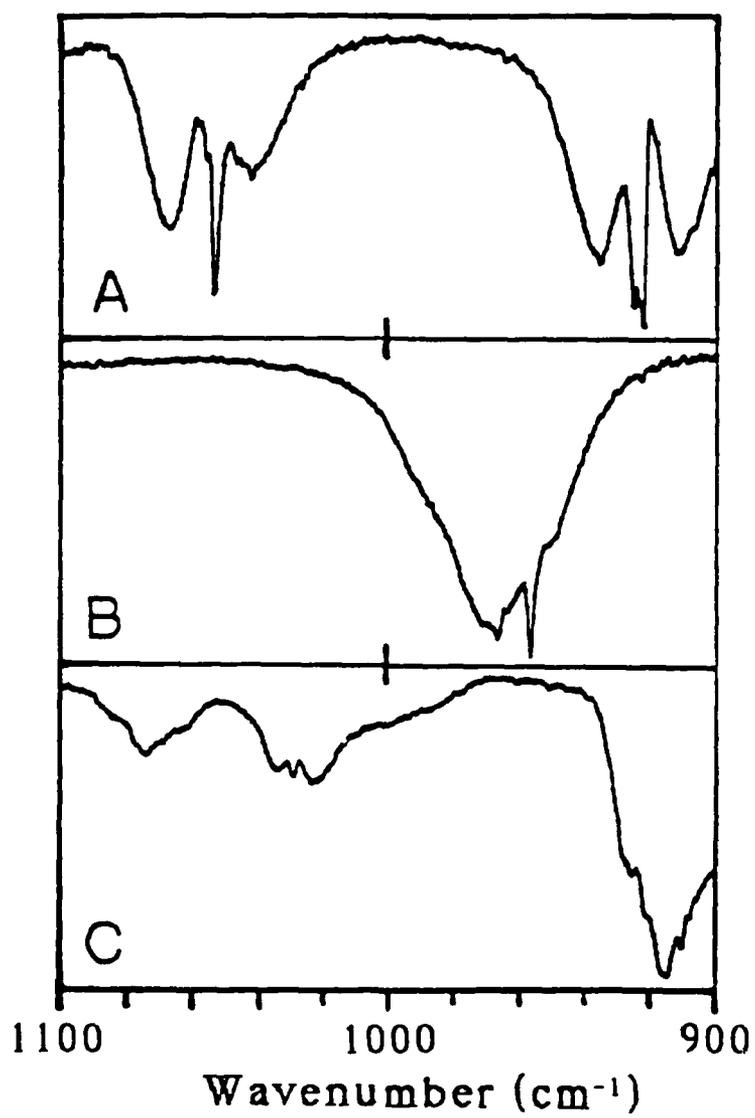


Figure 1. Gas phase-infrared spectra in the 1100-cm⁻¹ region.

- A. Propane, 200 torr
- B. n-butane, 200 torr
- C. n-pentane, 200 torr

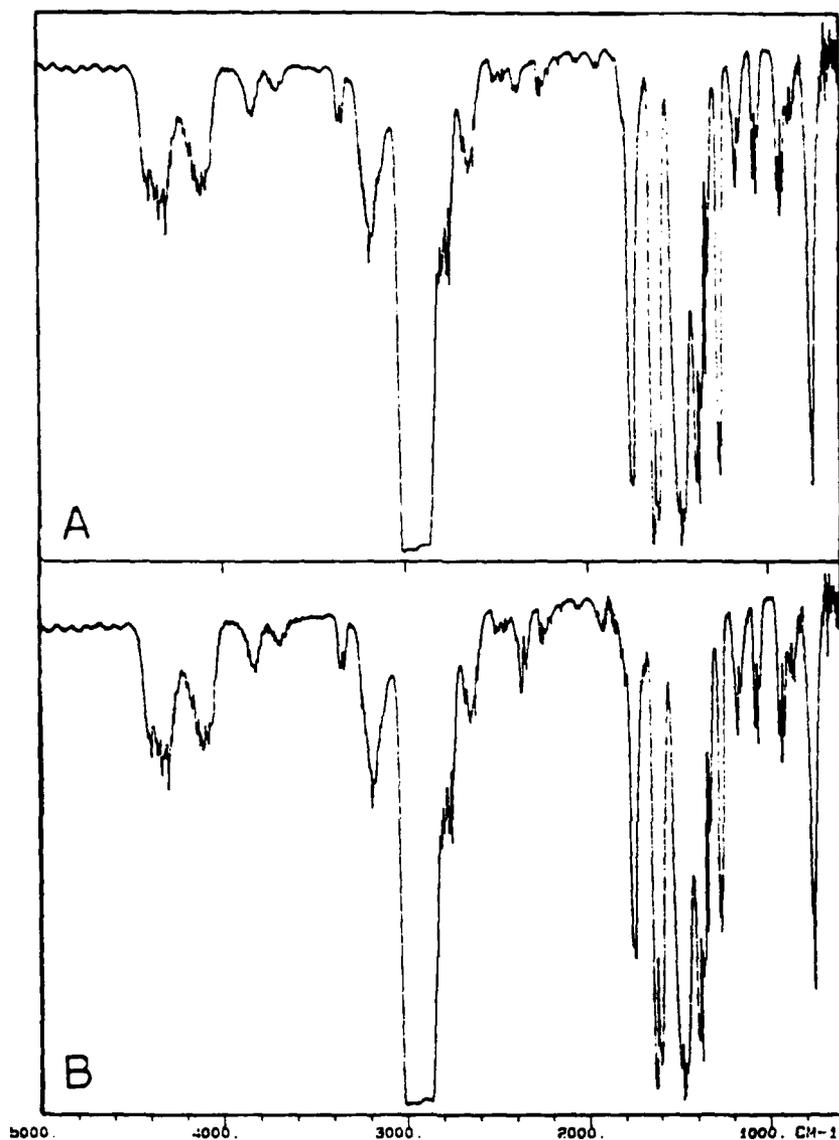


Figure 2. Gas phase mid-infrared spectra of propane/NO₂ mixtures before irradiation and the products resulting from laser excitation.

- A. Spectra of 470 torr propane and 30 torr NO₂
- B. Spectra of products after CO₂ laser excitation of the mixture in Fig. 2A using the following conditions: P(40) of (00⁰1-10⁰0), 924.9749 cm⁻¹; 60 sec; and 82 W/cm².

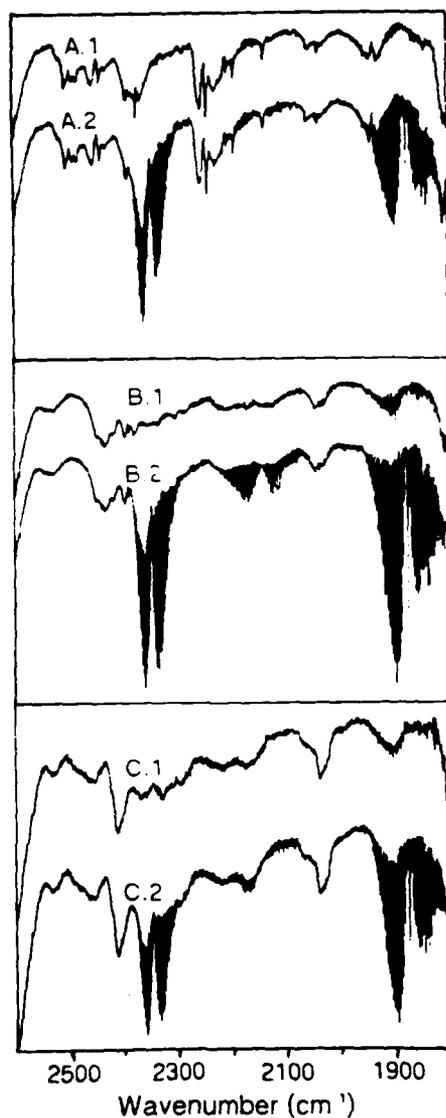


Figure 3. Gas phase infrared spectra of hydrocarbon/ NO_2 mixtures and the products resulting from laser excitation.

- A.1 Spectra of propane, 470 torr, and NO_2 , 30 torr
- A.2 Spectra of products formed by CO_2 laser excitation of the mixture described in Fig. 3A.1 under the following conditions: P(40) of (00⁰1-10⁰0), 924.9749 cm^{-1} ; 60 sec; and 82 W/cm^2 .
- B.1 Spectra of n-butane, 220 torr, and NO_2 , 20 torr
- B.2 Spectra of product formed by CO_2 laser excitation of the mixture described in Fig. 3B.1 under the following conditions: P(6) of (00⁰1-10⁰0), 956.1857 cm^{-1} ; 30 sec; and 75 W/cm^2 .
- C.1 Spectra of n-pentane, 200 torr, and NO_2 , 20 torr
- C.2 Spectra of products formed by CO_2 laser excitation of the mixture described in 3C.1 under the following conditions: P(40) of (00⁰1-10⁰0), 924.9749 cm^{-1} ; 30 sec; and 75 W/cm^2 .

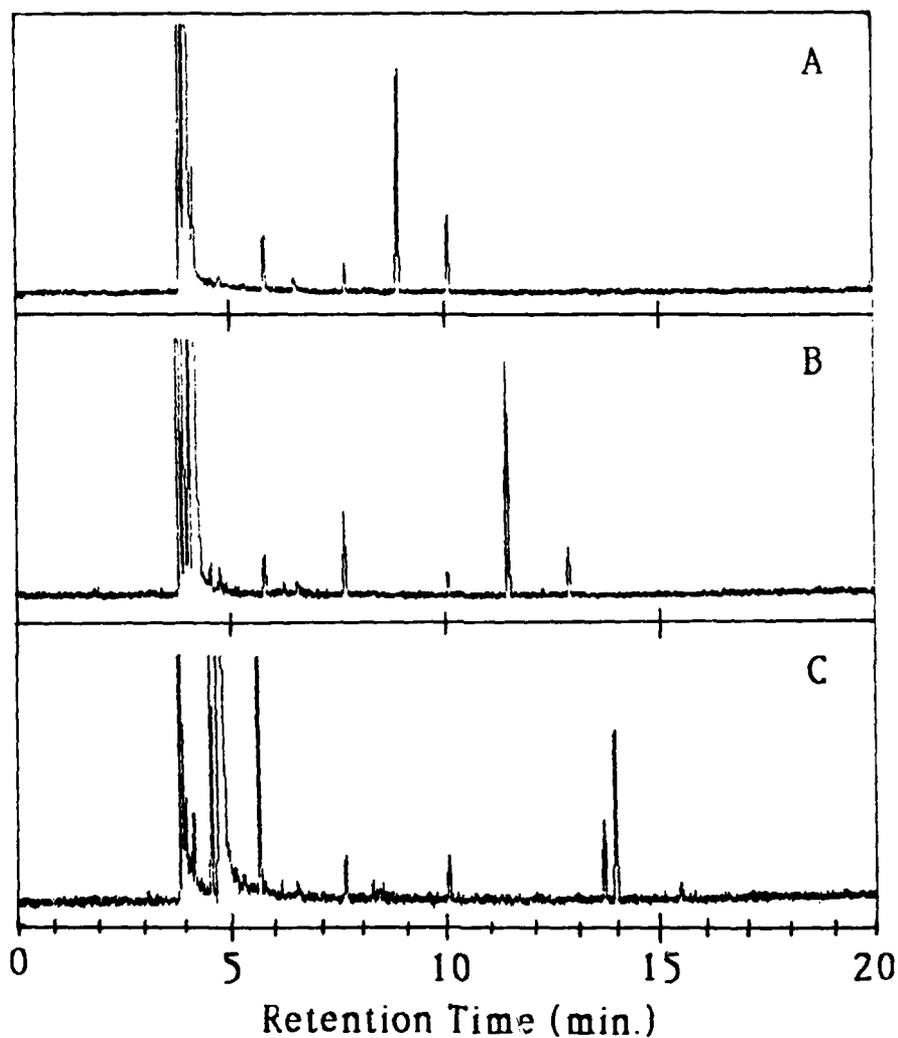


Figure 4. Gas chromatograms from the analysis of product mixes produced by the CO_2 laser excitation of hydrocarbon/ NO_2 mixtures under the following conditions:

- A. Propane, 550 torr, NO_2 , 30 torr: P(40) of $(00^0_1-10^0_0)$, 924.9749 cm^{-1} ; 60 sec; and 82 W/cm^2 .
- B. n-butane, 220 torr, NO_2 , 20 torr: P(6) of $(00^0_1-10^0_0)$, 956.1857 cm^{-1} ; 30 sec; and 75 W/cm^2 .
- C. n-pentane, 200 torr, NO_2 , 20 torr: P(40) of $(00^0_1-10^0_0)$, 924.9749 cm^{-1} ; 30 sec; and 75 W/cm^2 .

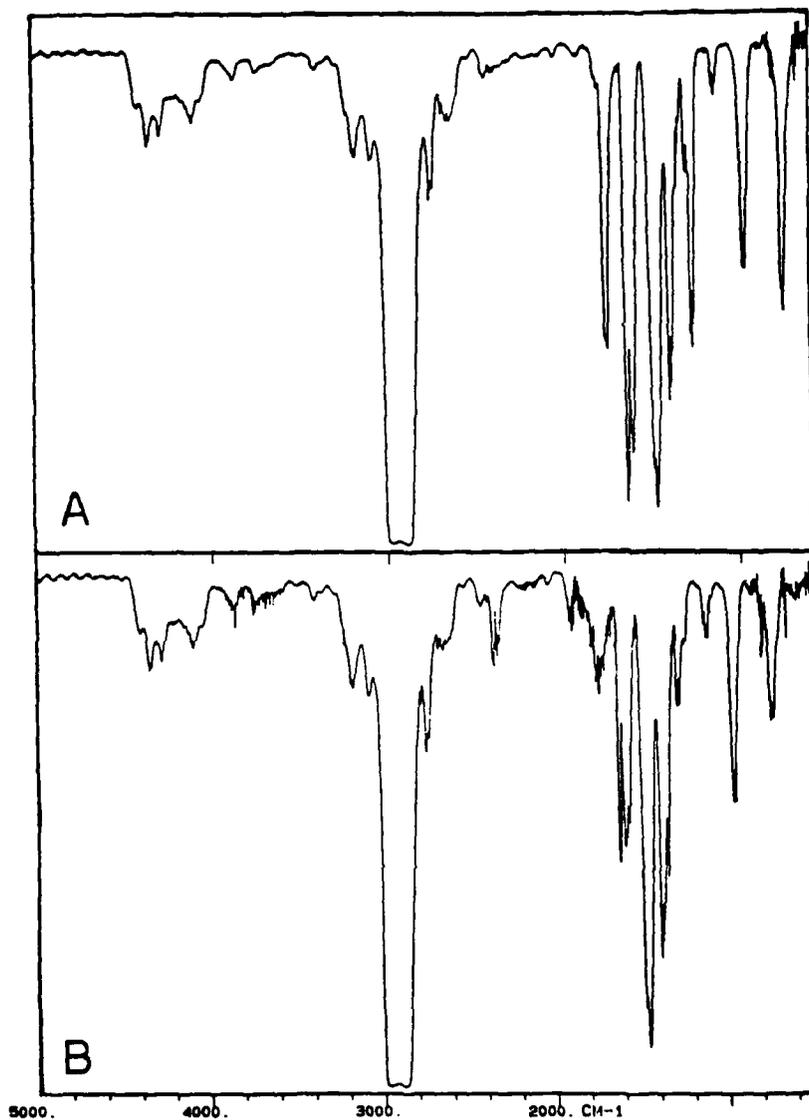


Figure 5. Gas phase mid-infrared spectra of butane/ NO_2 mixtures before excitation and products resulting from the CO_2 laser excitation of this mixture.

- A. Spectra of n-butane, 220 torr, and NO_2 , 20 torr.
- B. Spectra of products formed from the CO_2 laser excitation of the mixture in 5A under the following conditions: P(6) of $(00^0_1-10^0_0)$, 956.1857 cm^{-1} ; 30 sec; and 75 W/cm^2 .

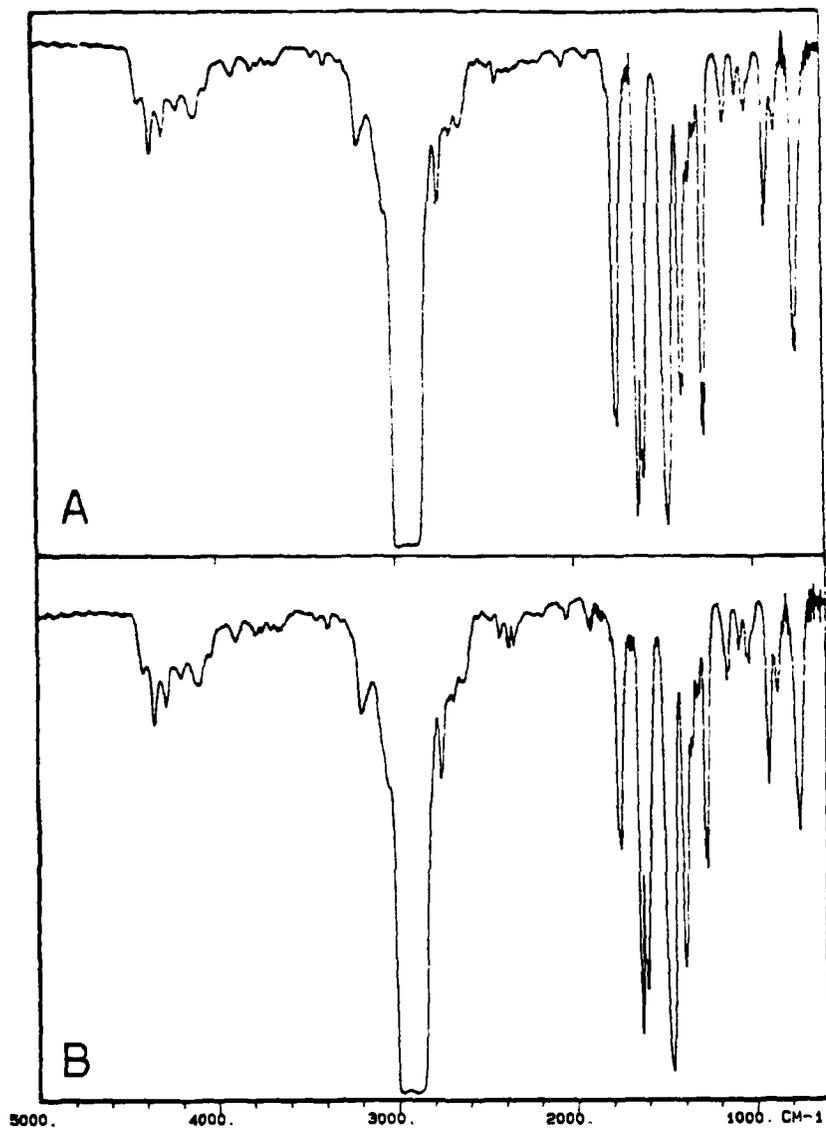


Figure 6. Gas phase mid-infrared spectra of pentane/NO₂ mixtures before excitation and the products formed by the CO₂ laser excitation of this mixture.

- A. Spectra of n-pentane, 220 torr, and NO₂, 20 torr.
- B. Spectra of products formed by the CO₂ laser excitation of the mixture in 6A under the following conditions: P(40) of (00⁰1-10⁰0), 924.9749 cm⁻¹; 30 sec; and 75 W/cm².

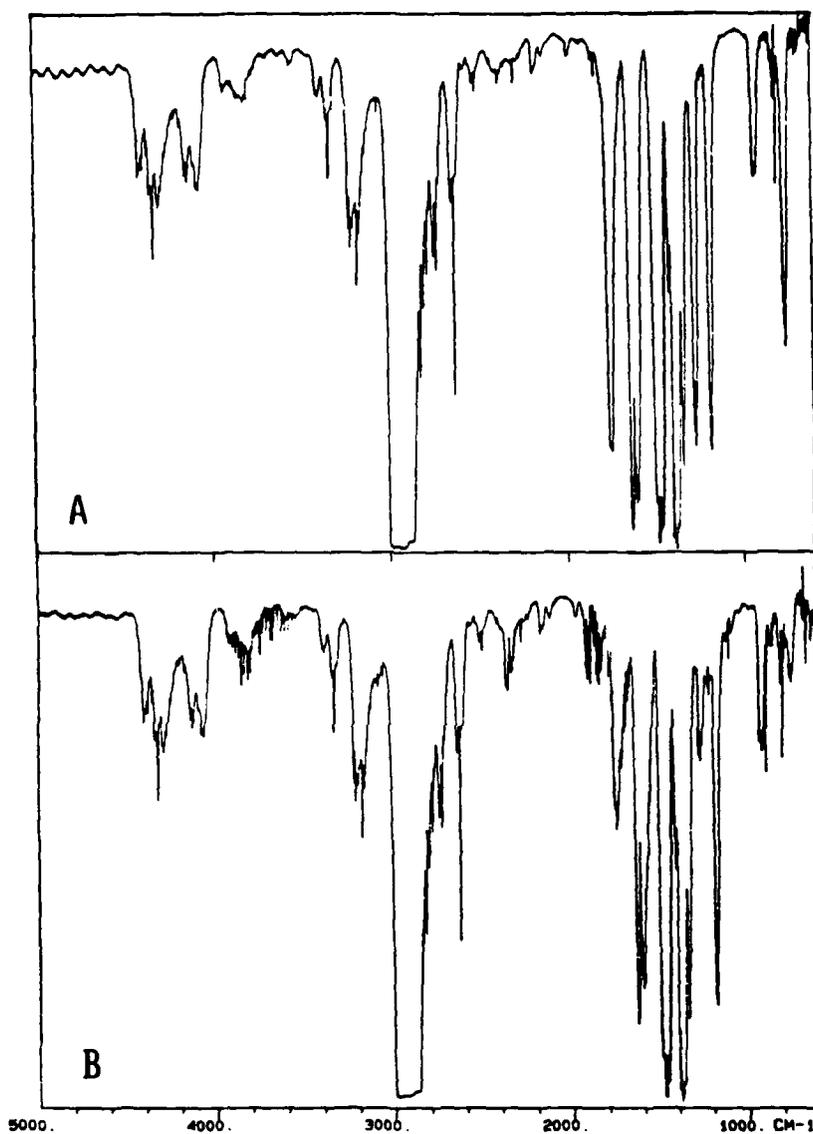


Figure 7. Gas phase mid-infrared spectra of isobutane/ NO_2 mixtures before excitation and products resulting from the CO_2 laser excitation of this mixture.

- A. Spectra of isobutane, 350 torr, and NO_2 , 25 torr.
- B. Spectra of products formed from the CO_2 laser excitation of the mixture in 7A under the following conditions: $P(40)$ of $(00^0_1-10^0_0)$, 924.9749 cm^{-1} ; 60 sec; and 100 W/cm^2 .

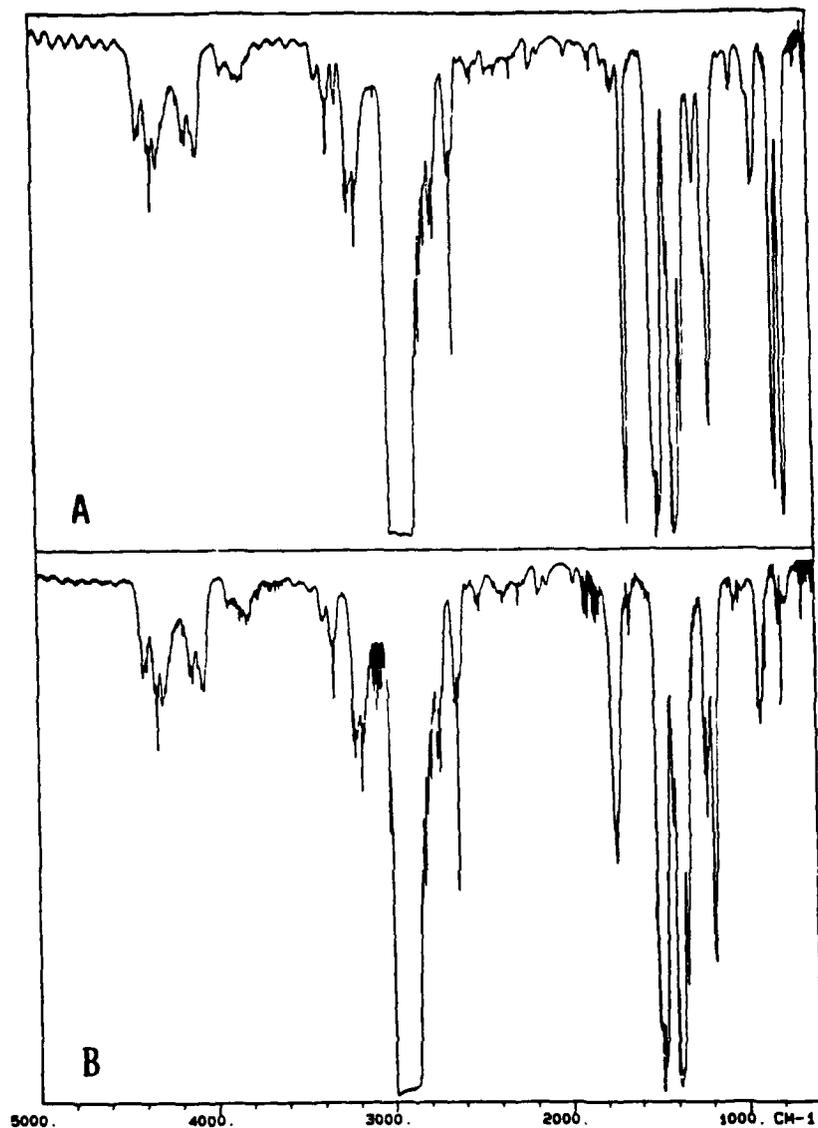


Figure 8. Gas phase mid-infrared spectra of t-butyl nitrite/isobutane mixtures before excitation and the products forms by the CO₂ laser excitation of this mixture.

- A. Spectra of t-butyl nitrite, 11 torr, and isobutane, 300 torr.
- B. Spectra of products formed by the CO₂ laser excitation of the mixture in 6A under the following conditions: P(40) of (00⁰1-10⁰0), 924.9749 cm⁻¹, 60 sec; and 100 W/cm².

TABLE 1. Frequencies (cm^{-1})* and Assignment for the Infrared Bands Observed in the Laser-Induced Reaction of Propane and NO_2

| Propane | $\text{NO}_2/\text{N}_2\text{O}_4$ | Mixture Before Irradiation | Mixture After Irradiation | Identity | Ref. |
|-----------|------------------------------------|----------------------------|---------------------------|------------------------|------|
| 3343-3186 | | 3344-3186 | 3343-3186 | Propane | |
| Offscale | 2918 | Offscale | Offscale | | |
| Offscale | 2890 | Offscale | Offscale | | |
| 2828-2374 | | 2828-2374 | 2828-2374 | Propane | |
| | | | 2348 | CO_2 | 14 |
| 2243-2193 | | 2242-2193 | 2243-2193 | Propane | |
| 2138 | | 2138 | 2138 | Propane | |
| | | | 2128-2103 | CO | 14 |
| 2038 | | 2039 | 2038 | Propane | |
| 1938 | | 1938 | 1938 | Propane | |
| | | | 1876 | NO | 15 |
| | 1750 | 1750 | 1750 | N_2O_4 | 16 |
| | 1617 | 1617 | 1617 | NO_2 | 8 |
| 1472 | | 1471 | 1472 | Propane | 4 |
| 1394 | | 1394 | 1394 | Propane | 4 |
| 1376 | | 1376 | 1376 | Propane | 4 |
| 1338 | | 1337 | 1338 | Propane | 4 |
| | 1261 | 1261 | 1261 | N_2O_4 | 16 |
| 1191 | | 1190 | 1190 | Propane | 4 |
| 1158 | | 1158 | 1158 | Propane | 4 |
| 1053 | | 1053 | 1053 | Propane | 4 |
| 922 | | 925 | 925 | Propane | 4 |

TABLE 1. Frequencies (cm^{-1})* and Assignment for the Infrared Bands Observed in the Laser-Induced Reaction of Propane and NO_2
(cont'd)

| Propane | $\text{NO}_2/\text{N}_2\text{O}_4$ | Mixture Before Irradiation | Mixture After Irradiation | Identity | Ref. |
|---------|------------------------------------|----------------------------|---------------------------|-------------------------------------|--------|
| 869 | | 869 | 869 | Propane | 4 |
| | 758 | 757 | | $\text{NO}_2, \text{N}_2\text{O}_4$ | 8,16 |
| | 755 | 755 | | $\text{NO}_2, \text{N}_2\text{O}_4$ | 8,16 |
| | 750 | 750 | 750 | $\text{NO}_2, \text{N}_2\text{O}_4$ | 8,16 |
| 748 | 747 | 748 | 748 | $\text{NO}_2, \text{N}_2\text{O}_4$ | 4,8,16 |
| | | | | Propane | |

* Only fundamentals and major bands in the region from $3500\text{--}500\text{ cm}^{-1}$ are listed.

TABLE 2. Summary of GC-MS Data from the Analysis of the Products of the Laser-Induced Nitration of Propane with NO₂.

| Retention Time | Area | Area % | Ratio % | Probable Identification | Amount Torr* |
|----------------|---------|--------|---------|-------------------------|--------------|
| 3.921 | 9145594 | 2.03 | 2.12 | More than 1 component | --- |
| 4.018 | 4.310E8 | 95.78 | 100.00 | Propane | --- |
| 4.227 | 3090683 | 0.69 | 0.72 | Butane ? | --- |
| 4.774 | 212605 | 0.05 | 0.05 | ?? | --- |
| 4.831 | 334010 | 0.07 | 0.08 | ?? | --- |
| 5.372 | 314391 | 0.07 | 0.07 | ?? | --- |
| 5.840 | 781757 | 0.17 | 0.18 | Nitromethane | 1.5 |
| 6.550 | 314698 | 0.07 | 0.07 | ?? | --- |
| 7.688 | 501706 | 0.11 | 0.12 | Nitroethane | 0.8 |
| 8.922 | 3268045 | 0.73 | 0.76 | 2-nitropropane | 1.7 |
| 10.10 | 1040723 | 0.23 | 0.24 | 1-nitropropane | 0.7 |

* Conditions employed in this reaction were: propane pressure, 470 torr; NO₂ pressure, 30 torr; laser line, P(40) of (00⁰1-10⁰); laser power, 82 W/cm²; irradiation time, 60 sec. The estimated amounts of nitroparaffin products are based on calibration of the instrument response when known pressures of these component were placed in the reaction cell and injected through the gas sampling loop.

TABLE 3. Summary of GC-MS Data from the Analysis of the Products of the Laser-Induced Nitration of Butane with NO₂.

| Retention Time | Area | Area % | Ratio % | Probable Identification | Amount Torr* |
|----------------|----------|--------|---------|-------------------------|--------------|
| 3.916 | 11882909 | 3.14 | 3.44 | More than 1 component | --- |
| 4.027 | 4948455 | 1.31 | 1.44 | Butane impurity | --- |
| 4.095 | 504639 | 0.13 | 0.15 | ?? | --- |
| 4.147 | 4432754 | 1.17 | 1.28 | ?? | --- |
| 4.242 | 3.459E8 | 91.27 | 100.00 | Butane | --- |
| 4.621 | 861449 | 0.23 | 0.25 | ?? | --- |
| 4.835 | 666027 | 0.18 | 0.19 | ?? | --- |
| 5.836 | 892597 | 0.24 | 0.26 | Nitromethane | 1.1 |
| 6.605 | 178691 | 0.05 | 0.05 | ?? | --- |
| 7.681 | 1782231 | 0.47 | 0.52 | Nitroethane | 1.4 |
| 10.10 | 556120 | 0.15 | 0.16 | 1-nitropropane | 0.5 |
| 11.49 | 4668849 | 1.23 | 1.35 | 2-nitrobutane | 4.0 |
| 12.93 | 1032901 | 0.27 | 0.30 | 1-nitrobutane | 0.9 |

* Conditions employed in this reaction were: n-butane pressure, 220 torr; NO₂ pressure, 20 torr; laser line, P(6) of (00⁰1-10⁰); laser power, 75 w/cm²; irradiation time, 30 sec. The estimated amounts of nitroparaffin products, except 2-nitrobutane, were based on calibration of the instrument response when known pressures of these compounds were placed in the reaction cell and injected through the gas sampling loop. The pressure of 2-nitrobutane produced is estimated based on the calibration of 1-nitrobutane.

TABLE 4. Frequencies (cm^{-1})* and Assignment for the Infrared Bands Observed in the Laser-Induced Reaction of Butane and NO_2

| Butane | $\text{NO}_2/\text{N}_2\text{O}_4$ | Mixture Before Irradiation | Mixture After Irradiation | Identity | Ref. |
|-----------|------------------------------------|----------------------------|---------------------------|----------|------|
| 3291-3085 | | 3293-3087 | 3297-3085 | Butane | |
| Offscale | 2918 | Offscale | Offscale | | |
| Offscale | 2890 | Offscale | Offscale | | |
| | | | 2817 | | |
| | | | 2815 | | |
| | | | 2812 | | |
| | | | 2810 | | |
| | | | 2807 | | |
| | | | 2805 | | |
| | | | 2803 | | |
| | | | 2802 | | |
| | | | 2797 | | |
| 2795 | | 2794 | 2794 | Butane | |
| | | | 2790 | | |
| | | | 2787 | | |
| | | | 2784 | | |
| | | | 2781 | | |
| | | | 2779 | | |
| | | | 2775 | | |
| | | | 2773 | | |
| | | | 2770 | | |
| | | | 2766 | | |
| | | | 2764 | | |
| | | | 2761 | | |

TABLE 4. Frequencies (cm^{-1})* and Assignment for the Infrared Bands Observed in the Laser-Induced Reaction of Butane and NO_2 (cont'd)

| Butane | $\text{NO}_2/\text{N}_2\text{O}_4$ | Mixture Before Irradiation | Mixture After Irradiation | Identity | Ref. |
|-----------|------------------------------------|----------------------------|---------------------------|---------------------------|------|
| | | | 2759 | | |
| | | | 2755 | | |
| | | | 2753 | | |
| | | | 2752 | | |
| 2743 | | 2743 | 2742 | Butane | |
| 2682 | | 2682 | 2683 | Butane | |
| | | | 2668 | | |
| 2654-2389 | | 2653-2389 | 2652-2390 | Butane | |
| | | | 2348 | CO_2 | 14 |
| | | | 2143 | CO | 14 |
| 2033 | | 2037 | 2037 | Butane | |
| 1902 | | 1900 | 1900 | Butane | |
| | | | 1876 | NO | 15 |
| | 1750 | 1750 | 1746 | N_2O_4 | 16 |
| | 1617 | 1617 | 1617 | NO_2 | 8 |
| | | | 1570 | Nitroalkanes | 5-7 |
| 1471 | | 1471 | 1471 | Butane | 4 |
| 1466 | | 1466 | 1466 | Butane | 4 |
| 1462 | | 1462 | 1462 | Butane | 4 |
| 1383 | | 1383 | 1383 | Butane | 4 |
| | | | 1351 | KNO_3 on windows | 17 |

TABLE 4. Frequencies (cm^{-1})^{*} and Assignment for the Infrared Bands Observed in the Laser-Induced Reaction of Butane and NO_2 (cont'd)

| Butane | $\text{NO}_2/\text{N}_2\text{O}_4$ | Mixture Before Irradiation | Mixture After Irradiation | Identity | Ref. |
|--------|------------------------------------|----------------------------|---------------------------|---|--------|
| 1344 | | 1344 | 1344 | Butane | 4 |
| 1294 | | 1295 | 1295 | Butane | 4 |
| | 1261 | 1261 | 1264 | N_2O_4 | 16 |
| 1135 | | 1135 | 1135 | Butane | 4 |
| | | | 1105 | | |
| | | | 1076 | | |
| 957 | | 957 | 957 | Butane | 4 |
| | 758 | 758 | | $\text{N}_2\text{O}_4, \text{NO}_2$ | 8,16 |
| | 755 | 755 | | $\text{N}_2\text{O}_4, \text{NO}_2$ | 8,16 |
| | 750 | 750 | | $\text{N}_2\text{O}_4, \text{NO}_2$ | 8,16 |
| 747 | 747 | 748 | 747 | Butane, $\text{NO}_2, \text{N}_2\text{O}_4$ | 4,8,16 |
| 733 | | 733 | 733 | Butane | 4 |

^{*}Only fundamentals and major bands in the region from 3500-500 cm^{-1} are listed.

TABLE 5. Summary of GC-MS Data from the Analysis of the Products of the Laser-Induced Nitration of n-Pentane with NO₂.

| Retention Time | Area | Area % | Ratio % | Probable Identification | Amount Torr* |
|----------------|----------|--------|---------|-------------------------|--------------|
| 3.905 | 5002700 | 1.25 | 1.34 | More than 1 component | --- |
| 4.010 | 1404895 | 0.35 | 0.38 | Pentane impurity plus? | --- |
| 4.075 | 408476 | 0.10 | 0.11 | Pentane impurity plus? | --- |
| 4.129 | 491759 | 0.12 | 0.13 | Pentane impurity plus? | --- |
| 4.203 | 1288258 | 0.33 | 0.34 | Pentane impurity plus? | --- |
| 4.605 | 3178313 | 0.80 | 0.85 | Pentane impurity plus? | --- |
| 4.792 | 3.7409E8 | 94.40 | 100.00 | Pentane | --- |
| 4.887 | 1220945 | 0.31 | 0.33 | ?? | --- |
| 5.134 | 279689 | 0.07 | 0.07 | ?? | --- |
| 5.181 | 382545 | 0.10 | 0.10 | ?? | --- |
| 5.684 | 3496246 | 0.88 | 0.93 | Pentane impurity | --- |
| 7.663 | 528792 | 0.13 | 0.14 | Nitroethane | 0.8 |
| 8.274 | 226095 | 0.06 | 0.06 | ?? | --- |
| 10.08 | 587932 | 0.15 | 0.16 | 1-nitropropane | 0.5 |
| 13.69 | 993117 | 0.25 | 0.27 | 3-nitropentane | 0.9 |
| 13.98 | 2070157 | 0.52 | 0.55 | 2-nitropentane | 1.9 |
| 15.49 | 248895 | 0.06 | 0.07 | 1-nitropentane | 0.6 |

* Conditions employed in this reaction were: n-pentane pressure, 220 torr; NO₂ pressure, 20 torr; laser line, P(40) of (00⁰1-10⁰0); laser power, 75 w/cm²; irradiation time, 30 sec. The estimated amounts of nitroparaffin products, except 2-nitropentane and 3-nitropentane, are based on calibration of the instrument response when known pressures of these components were placed in the reaction cell and injected through the gas sampling loop. The pressures of 2-nitropentane and 3-nitropentane produced is estimated based on the calibration of 1-nitropentane.

TABLE 6. Frequencies (cm^{-1})* and Assignment for the Infrared Bands Observed in the Laser-Induced Reaction of Pentane and NO_2

| Pentane | $\text{NO}_2/\text{N}_2\text{O}_4$ | Mixture Before Irradiation | Mixture After Irradiation | Identity | Ref. |
|-----------|------------------------------------|----------------------------|---------------------------|---------------------------------|------|
| 3375 | | 3375 | 3378 | Pentane | |
| 3190 | | 3191 | 3190 | Pentane | |
| Offscale | 2918 | Offscale | Offscale | | |
| Offscale | 2890 | Offscale | Offscale | | |
| | | | 2781 | | |
| | | | 2779 | | |
| | | | 2766 | | |
| 2749-2415 | | 2749-2414 | 2749-2415 | Pentane | |
| | | | 2348 | CO_2 | 14 |
| | | | 2259-2086 | CO | 14 |
| 2041 | | 2041 | 2040 | Pentane | |
| 1907 | | 1906 | | Pentane | |
| | | | 1876 | NO | 15 |
| | 1750 | 1750 | 1750 | N_2O_4 | 16 |
| | 1617 | 1617 | 1617 | NO_2 | 8 |
| 1465 | | 1464 | 1465 | Pentane | 4 |
| 1383 | | 1383 | 1385 | Pentane | 4 |
| 1345 | | 1346 | 1346 | Pentane | 4 |
| 1311 | | 1311 | 1310 | Pentane | 4 |
| 1261 | 1261 | 1261 | 1261 | Pentane, N_2O_4 | 4,16 |
| 1140 | | 1139 | 1139 | Pentane | 4 |
| 1074 | | 1074 | 1075 | Pentane | 4 |

TABLE 6. Frequencies (cm^{-1})* and Assignment for the Infrared Bands Observed in the Laser-Induced Reaction of Pentane and NO_2 (cont'd)

| Pentane | $\text{NO}_2/\text{N}_2\text{O}_4$ | Mixture Before Irradiation | Mixture After Irradiation | Identity | Ref. |
|---------|------------------------------------|----------------------------|---------------------------|-------------------------------------|--------|
| 1029 | | 1029 | 1029 | Pentane | 4 |
| 915 | | 915 | 916 | Pentane | 4 |
| 864 | | 862 | 862 | Pentane | 4 |
| | 758 | 758 | | $\text{NO}_2, \text{N}_2\text{O}_4$ | 8,16 |
| | 755 | 755 | 755 | $\text{NO}_2, \text{N}_2\text{O}_4$ | 8,16 |
| | 750 | 750 | 750 | $\text{NO}_2, \text{N}_2\text{O}_4$ | 8,16 |
| | 747 | 748 | 748 | $\text{NO}_2, \text{N}_2\text{O}_4$ | 8,16 |
| 739 | 742 | 741 | 742 | $\text{NO}_2, \text{N}_2\text{O}_4$ | 4,8,16 |
| | | | | Pentane | |
| 733 | | | 733 | Pentane | 4 |
| 728 | | 728 | 729 | Pentane | 4 |

* Only fundamentals and major bands in the region from $3500\text{-}500\text{ cm}^{-1}$ are listed.

TABLE 7. Summary of GC-MS Data from the Analysis of the Products of the Laser-Induced Nitration of Isobutane with NO₂

| Retention Time | Area | Area % | Ratio % | Probable Identification | Amount Torr* |
|----------------|----------|--------|---------|-------------------------|--------------|
| 3.869 | 7123714 | 2.24 | 2.49 | More than 1 component | |
| 3.976 | 1208879 | 0.38 | 0.42 | 1-propene | |
| 4.087 | 2.8593E8 | 89.96 | 100.00 | Isobutane | |
| 4.177 | 13751785 | 4.33 | 4.81 | 2-methylpropene | |
| 4.764 | 3313667 | 1.04 | 1.16 | Acetone | |
| 5.780 | 896764 | 0.28 | 0.31 | Nitromethane | 1.6 |
| 6.533 | 217142 | 0.07 | 0.08 | ?? | |
| 8.857 | 579598 | 0.18 | 0.2 | 2-nitropropane | 0.6 |
| 10.064 | 3561312 | 1.12 | 1.25 | 2-methyl-2-nitropropane | 2.5 |
| 11.475 | 1248439 | 0.39 | 0.44 | 1-nitro-2-methylpropane | 0.1 |

* Conditions employed in this reaction were: isobutane pressure, 350 torr; NO₂ pressure, 25 torr; laser line, P(40) of (00⁰1) - (00⁰0); laser power, 100 W/cm²; irradiation time, 60 sec. The estimated amounts of nitroparaffin products, except 2-nitrobutane, are based on calibration of the instrument response when known pressures of these components were placed in the reaction cell and injected through the gas sampling loop. The pressure of 2-nitrobutane produced is estimated based on the calibration of 1-nitrobutane.

TABLE 8. Frequencies (cm^{-1}) and Assignment for the Infrared Bands Observed in the Laser-Induced Reaction of Isobutane and NO_2

| Isobutane | $\text{NO}_2/\text{N}_2\text{O}_4$ | Mixture Before Irradiation | Mixture After Irradiation | Identity | Ref. |
|-----------|------------------------------------|----------------------------|--|---------------------------------------|----------|
| 3388-3163 | | 3388-3163 | 3388-3163 3060 | Isobutane | |
| Offscal | 2918 | Offscale | Offscale | | |
| Offscale | 2890 | Offscale | Offscale | | |
| 2840-2372 | | 2840-2369 | 2840-2504 2348 | Isobutane CO_2 | 14 |
| 2285 | | 2285 | 2285 | Isobutane | 9 |
| 2177 | | 2177 | 2176 2173-2082 | Isobutane CO | 9 14 |
| 1973 | | 1974 | 1973 1876 | Isobutane NO | 9 15 |
| 1828 | | 1823 | | Isobutane | 9 |
| | 1750 | 1750 | 1746 1717 1700 1696 1685 1675 1653 | N_2O_4 Isobutane ? | 16 18 |
| | 1617 | 1617 | 1617 | NO_2 | 8 |
| 1477 | | 1476 | 1480 | Isobutane | 9 |
| 1411 | | 1410 | 1409 | Isobutane | 9 |

TABLE 8. Frequencies (cm^{-1}) and Assignment for the Infrared Bands Observed in the Laser-Induced Reaction of Isobutane and NO_2 (cont'd)

| Isobutane | $\text{NO}_2/\text{N}_2\text{O}_4$ | Mixture Before Irradiation | Mixture After Irradiation | Identity | Ref. |
|-----------|------------------------------------|----------------------------|---------------------------|-----------------------------------|------|
| 1396 | | 1396 | 1396 | Isobutane | 9 |
| 1376 | | 1379 | 1381 | Isobutane | 9 |
| 1334 | | 1334 | 1334 | Isobutane | 9 |
| 1326 | | 1326 | 1326 | Isobutane | 9 |
| | 1261 | 1261 | 1261 | N_2O_4 | 16 |
| | | | 1216 | Acetone | 19 |
| 1174 | | 1174 | 1174 | Isobutane | 9 |
| | | | 1105 | | |
| 924 | | 924 | 925 | Isobutane | 9 |
| 909 | | 912 | 911 | Isobutane | 9 |
| | | | 890 | Isobutene | 18 |
| | 758 | | | | |
| | 755 | ~ 755 | | | |
| | 750 | ~ 750 | ~ 750 | $\text{NO}_2\text{N}_2\text{O}_4$ | 8,16 |
| | 747 | | | | |
| | 742 | | | | |

TABLE 9. Summary of GC-MS Data from the Analysis of the Products of the Laser-Induced Decomposition of t-butyl nitrite Using Isobutane as a Sensitizer*.

| Retention Time | Area | Area % | Ratio % | Probable Identification |
|----------------|----------|--------|---------|---|
| 3.827 | 4394204 | 1.50 | 1.70 | More than 1 component |
| 3.933 | 1608272 | 0.55 | 0.62 | 1-propene ? |
| 4.043 | 2.5857E8 | 88.25 | 100.00 | Isobutane |
| 4.132 | 6629786 | 2.26 | 2.56 | 2-methylpropene |
| 4.199 | 1759781 | 0.60 | 0.68 | ?? |
| 4.512 | 159017 | 0.05 | 0.06 | ?? |
| 4.703 | 17763940 | 6.06 | 6.87 | Acetone |
| 5.081 | 870249 | 0.30 | 0.34 | 2-methyl-2-propanol (impurity in t-butyl nitrite) |
| 5.570 | 705918 | 0.24 | 0.27 | t-butyl nitrite |
| 9.088 | 358155 | 0.17 | 0.14 | ?? |
| 9.123 | 180050 | 0.06 | 0.07 | ?? |

* Conditions employed in this reaction were: Isobutane pressure, 300 torr; t-butyl nitrite pressure, 11 torr; laser line, P(40) of (00⁰1) - (00⁰0); laser power, 100 W/cm²; irradiation time, 60 sec.

TABLE 10. Frequencies (cm^{-1}) and Assignment for the Infrared Bands Observed in the Laser-Induced Decomposition of t-butylinitrite Using Isobutane as a Sensitizer

| Isobutane | t-butylinitrite | Mixture Before Irradiation | Mixture After Irradiation | Identity | Ref. |
|-----------|-----------------|----------------------------|---------------------------|-----------------------------|------|
| 3388 | | 3389 | 3388 | Isobutane | |
| 3332 | | 3332 | 3332 | Isobutane | |
| | 3278 | 3277 | | t-butylinitrite | 10 |
| 3223-3163 | | 3223-3162 | 3221-3163 | Isobutane | |
| | | | 3140-3108 | Methane | 20 |
| Offscale | 2989 | Offscale | Offscale | | 10 |
| 2840-2504 | | 2840-2504 | 2840-2504 | Isobutane | 9 |
| | 2464 | 2464 | | t-butylinitrite | 10 |
| | 2422 | 2421 | | t-butylinitrite | 10 |
| 2372-1973 | | 2369-1977 | 2369-1977 | Isobutane | 9 |
| | | | 1876 | NO | 15 |
| 1828 | | 1828 | | Isobutane | 9 |
| | | | 1740 | Acetone | 19 |
| | | | 1725 | Acetone | 19 |
| | 1663 | 1663 | | t-butylinitrite | 10 |
| | | | ~ 1653w | | |
| 1477 | 1472 | 1479 | 1479 | Isobutane | 9 |
| 1411 | | | | | |
| 1396 | 1398 | 1396 | 1396 | Isobutane + t-butylinitrite | 9,10 |
| 1376 | 1375 | 1375 | 1375 | Isobutane + t-butylinitrite | 9,10 |
| 1334 | | 1334 | 1335 | Isobutane | 9 |

TABLE 10. Frequencies (cm^{-1}) and Assignment for the Infrared Bands Observed in the Laser-Induced Decomposition of t-butyl nitrite Using Isobutane as a Sensitizer (cont'd)

| Isobutane | t-butyl nitrite | Mixture Before Irradiation | Mixture After Irradiation | Identity | Ref. |
|-----------|-----------------|----------------------------|---------------------------|-----------------------------|------|
| 1326 | | 1326 | 1327 | Isobutane | 9 |
| | | | 1305 | Methane | 20 |
| | 1256 | 1256 | | t-butyl nitrite | 10 |
| | | | 1217 | Acetone | 19 |
| | 1205 | 1206 | | t-butyl nitrite | 10 |
| | 1201 | | | | |
| 1174 | | 1174 | 1174 | Isobutane | 9 |
| | | | ~1096 | Acetone | 19 |
| | | | 1061 | Isobutene | 18 |
| | 1039 | 10 | | t-butyl nitrite | 10 |
| | | | 1033 | | |
| | 952 | 952 | | t-butyl nitrite | 10 |
| 924 | 920 | 926 | 926 | Isobutane + t-butyl nitrite | 9,10 |
| 909 | | 914 | 912 | Isobutane | 9 |
| | | | 890 | Isobutene | 18 |
| | 810 | 811 | | t-butyl nitrite | 10 |
| | 763 | 764 | | t-butyl nitrite | 10 |

TABLE 11. Comparison of Nitroalkane Products from Laser-Induced Nitrations to Thermally-Induced²² Nitrations.

| <u>Hydrocarbon</u> | <u>Product</u> | <u>Mole %</u> | |
|--------------------|-----------------------------|-----------------------------|----------------------|
| | | <u>Thermal</u> [†] | <u>Laser-Induced</u> |
| Propane | Nitromethane | 22.0 (32.3) | 32 |
| | Nitroethane | 16.6 (24.2) | 17 |
| | 1-nitropropane | 13.2 (24.2) | 15 |
| | 2-nitropropane | 48.2 (19.3) | 36 |
| Butane | Nitromethane | 10.5 | 14 |
| | Nitroethane | 15.8 | 18 |
| | 1-nitropropane | 5.3 | 6 |
| | 1-nitrobutane | 24.2 | 11 |
| | 2-nitrobutane | 44.2 | 51 |
| Pentane | Nitromethane | 2.3 | *Not determined |
| | Nitroethane | 10.9 | 17 |
| | 1-nitropropane | 16.7 | 11 |
| | 1-nitrobutane | 12.8 | 0 |
| | 1-nitropentane | 18.9 | 13 |
| | 2-nitropentane | 18.2 | 40 |
| | 3-nitropentane | 20.2 | 19 |
| Isobutane | Nitromethane | (5.8) | 28 |
| | 2-nitropropane | (23.1) | 10 |
| | 2-methyl- 2-nitropropane | 99.0 (7.0) | 43 |
| | 2-methyl- 1-nitropropane | (64.1) | 19 |

Ref. 22. H. B. Hass and H. Shechter, *Ind. Eng. Chem.* **39**, 817 (1947) and references therein.

[†]The temperatures used in the thermally-induced nitrations (Ref. 17 above), were as follows: Propane: 505-10⁰C for first set of numbers; 790-50⁰C for numbers in parentheses. Butane: 420⁰C. Pentane: 400⁰C. Isobutane: 150⁰C for first set of numbers; 420⁰C for numbers in parentheses.

*An impurity of the pentane sample obscured any chromatographic peak from nitromethane.

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