Photonitration of Hydrocarbons with Lasers

MERLE E. UMSTEAD, JAMES W. FLEMING, AND M. C. LIN

Abstract—The photonitration of isobutane (i-C4H10) has been investigated in the 458-515 nm region with an argon-ion laser as the radiation source. t-Nitrobutane (t-C4H9NO2) was the major product. Its rate of production was linear with laser intensity and increased with increasing photon energy. Computer modeling of possible reaction steps indicated that the reaction is initiated by the direct abstraction of hydrogen from i-C4H10 by electronically excited NO2.

INTRODUCTION

THE vapor-phase nitration of hydrocarbons with NO2 requires temperatures of 200-400°C in order for the reaction to take place at an acceptable rate [1]. The principal products of these reactions are nitro compounds (R-ONO2) and nitrites (R-ONO), along with lesser quantities of other compounds such as nitrates (R-ONO2). The higher the nitration temperature, the more important side reactions become mainly due to oxidation. More C-C bonds are broken leading to lower molecular weight products. Clearly it is desirable to carry out a nitration at as low a temperature as possible in order to minimize unwanted side reactions.

Nitrations with NO2 have been carried out photochemically at room temperature. At the wavelengths used, the NO2 is the only light-absorbing reactant. Work on the photochemical nitration of benzene has been summarized by Bunbury [2], and a more recent investigation of the effect of O2 on this reaction has been reported by Watanabe, Ishikawa, and Ando [3]. Paraskevopoulos and Cvetanovic [4] and Blacet et al. [5] investigated the photochemical nitration of isobutane, and the former authors made a detailed analysis of the reaction products.

Practically all photochemical nitrations with NO2 have been carried out with short-wavelength radiation, usually that form a mercury lamp, which dissociates NO2 into NO and O atoms. The O atoms initiate the reaction by abstracting an H atom from the hydrocarbon (RH), and the reaction proceeds according to the following simplified scheme [4]:

\[
\begin{align*}
\text{NO}_2 + h\nu &\rightarrow O + NO \\
O + RH &\rightarrow R\cdot + OH \\
OH + RH &\rightarrow R\cdot + H_2O \\
R\cdot + NO_2 &\rightarrow RNO_2 \\
R\cdot + NO_2 &\rightarrow RONO.
\end{align*}
\]

(1) (2) (3) (4) (5)

Sato and Cvetanovic [6] determined the long-wavelength limit of the photooxidation of 1-butene by NO2. They found products of the reaction of O atoms with butene in the presence of the 404.7 nm Hg line, but none with the very intense 435.8 nm line. The energy of the 404.7 nm line is comparable to the bond dissociation energy of NO2 to form NO and O (3P) atoms. These results are in agreement with early determinations of the long-wavelength threshold for the photolysis of NO2 itself [7], [8].

Little work appears to have been done at \(\lambda > 436 \text{ nm} \), probably because the amount of reaction products produced under normal photochemical conditions is too low to be readily measurable. Even at \(\lambda < 436 \text{ nm} \), nitration experiments usually require several hours of irradiation as a minimum, and in some cases, months are required [2]. The availability of the intense radiation from lasers provides a means of investigating photochemical nitration reactions that are not feasible by ordinary means. In this paper we report the preliminary results of an investigation of the photochemical nitration of isobutane with radiation between 457.9 and 514.5 nm from an argon-ion laser.

EXPERIMENTAL

A Coherent Model 52 argon-ion laser was used to electronically excite the NO2. Mixtures of i-C4H10, NO2, and in some experiments He, were irradiated in a Pyrex cell, 52 cm long by 1 cm ID, enclosed by Pyrex windows at each end, and equipped with greaseless stopcocks. Except for the windows, the cell was enclosed in an opaque material to block radiation from the room fluorescent lights. The laser beam, about 1.5 mm in diameter, was directed along the axis of the cell and finally into a Coherent Model 201 power meter for intensity measurements.

After irradiation, the contents of the cell were expanded into a low-pressure gas-sampling loop [9] in a Beckman GC-4 gas chromatograph equipped with a flame-ionization detector, and analyzed for organic products. The column used was a 12 ft length of 4.8 mm OD stainless-steel tubing packed with 20 percent 1,2,3-tris(cyanoethoxy)propane on gas chrom RZ. The major reaction product, t-nitrobutane, C(CH3)3NO2, was identified by both infrared absorption spectroscopy and mass spectrometry.

The NO2 was obtained from Matheson and was purified by trap-to-trap distillation at 195 K to remove traces of N2O3. The isobutane was Phillips Research Grade and was thoroughly degassed at 195 K before use.

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RESULTS AND DISCUSSION

With 10 torr of a 1:1 mixture of NO₂ and C₄H₁₀ in the cell, only several minutes of 1 W irradiation with the 488 nm line was sufficient to convert a few percent of the reactants into nitration products. The large number of chromatographic peaks obtained from the product mixture indicated that fragmentation of the primary products was significant at the low pressures used. The major product formed was t-nitrobutane (C₄H₉NO₂). Other products tentatively identified by their chromatographic retention times were t-butyl nitrite, nitromethane, 2-nitropropane, and acetone. The presence of acetone can readily be explained by the well-known chemistry of alkyl nitrites and alkoxy radicals [1]. A number of as yet unidentified products were also present. Peaks attributed to alkyl nitrites showed signs of decomposition in the chromatographic column; hence they could not be measured quantitatively.

The production of t-C₄H₉NO₂ was found to be linear with time up to 45 min (2.6 percent yield, based on C₄H₁₀), the longest irradiation time used. Its formation was also linear with laser intensity, as is shown in Fig. 1. Fig. 2 illustrates the effect of the wavelength of the exciting laser line on the efficiency of t-C₄H₉NO₂ production. Clearly, the higher energy radiation is more effective.

The mechanism of the photochemical nitration of i-C₄H₁₀ in the 458–515 nm region has not yet been unequivocally determined. At these photon energies the dissociation of NO₂ into NO and O atoms can be excluded. The reaction may proceed by one of two possible mechanisms, initiated by either electronically excited NO₂ (denoted by NO₂*) or by NO₃ formed by the reaction of NO₂ with NO₂ (NO₂ + NO₂ → NO₃ + NO):

\[ i{-}C₄H₁₀ + NO₂* → t{-}C₄H₉ + HNO₂ \]  \hspace{1cm} (6)

\[ i{-}C₄H₁₀ + NO₃ → t{-}C₄H₉ + HNO₃ \]  \hspace{1cm} (7)

The nitrobutane product can be formed by reaction (4), t-C₄H₉ + NO₂.

In order to elucidate the mechanism of nitrobutane formation, we have carried out detailed computer modeling of the observed product yields and NO₂ disappearance rates as functions of time and laser power, using known rate constants for NO₂, NO₂+, NO₃, and NO reactions, and NO₂ quenching constants reported by Creel and Ross [10] and Herman et al. [11]. The results of these modeling computations strongly support the direct abstraction of hydrogen from i-C₄H₁₀ by NO₂* [reaction (6)] as the major initiation process. Herman et al. reported that the laser-enhanced oxidation of CO by NO₂ also proceeds by the direct reaction of NO₂ with CO [11]. They also calculated that the temperature rise of the gas due to laser heating was too small to significantly influence the reaction. This should also be true for our study, carried out under similar conditions. More detailed theoretical and experimental studies of this nitration process are still underway, with particular emphasis on the effects of reactant ratios and added gases.

This study points out the value of the laser in carrying out photochemical reactions that are impractical by conventional photochemical techniques. We are currently pursuing our investigation of laser nitration at the longer wavelengths in the hope that the different mechanism operating in this region might lead to a more selective means of nitration that could result in products that are difficult or impossible to obtain by conventional nitration methods.

REFERENCES

Laser Cleanup of H$_2$S from Synthesis Gas

HAO-LIN CHEN AND CHUCK BORZILERI

Abstract—Hydrogen sulfide at the 10 ppm level has been selectively stripped from a CO + H$_2$ synthesis gas by photolysis with an ArF laser. The sulfur in the atomic or radical form is irreversibly removed by a metal surface. Spectroscopic and quantum yield data are presented. An H$_2$S spectroscopic selectivity less than $10^7$ was measured in the 210-220 nm range, a wavelength range compatible with Raman-shifted ArF or KrF lasers. The laser purification method described here is a potential approach to achieve sulfur impurity levels greater than 0.1 ppm. This method is of potential industrial significance for extending the lifetime of syngas metal catalysts.

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The authors are with the Lawrence Livermore Laboratory, Livermore, CA 94550.

James W. Fleming received the B.S. degree in chemistry in 1974 from Wake Forest University, Winston-Salem, NC, and the Ph.D. in physical chemistry from the University of North Carolina, Chapel Hill.

In 1979 he was awarded a National Research Council Postdoctoral Research Associateship to the Naval Research Laboratory in Washington, DC, working with M. C. Lin and A. B. Harvey in the areas of gas phase chemical kinetics and CARS. His research interests are in the area of coherent anti-Stokes Raman scattering (CARS), laser approaches to gas phase reaction kinetics and laser induced chemistry.

Dr. Fleming is a member of the American Chemical Society and Sigma Xi.

M. C. Lin received the B.S. degree in chemistry from the Taiwan National Normal University, Taipei, Taiwan, in 1959, and the Ph.D. degree in physical chemistry from the University of Ottawa, Ottawa, Ont., Canada, in 1965. He spent the years 1965-1967 at the University of Ottawa as a Postdoctoral Research Fellow with Professor K. J. Laidler, working in the field of gas phase chemical kinetics.

In early 1970 he joined the Naval Research Laboratory, Washington, DC, as a Research Chemist and initiated the chemical laser program in the Chemistry Division. He is presently Head of the Chemical Kinetics Section, engaging in research related to gas phase reaction kinetics, laser chemistry, high energy materials, combustion chemistry of alternate fuels, and, more recently, the applications of lasers to heterogeneous catalytic processes. He has authored and coauthored over 50 articles in these and related fields.

Dr. Lin is a member of the American Chemical Society, the Optical Society of America, Sigma Xi, and the Combustion Institute, and a Fellow of the Washington Academy of Sciences.