

## Short Communication

Very low pressure photolysis of *tert*-butyl nitrite at 248 nm

PAULA L. TREVOR† and DAVID M. GOLDEN

Department of Chemical Kinetics, SRI International, Menlo Park, CA 94025 (U.S.A.)

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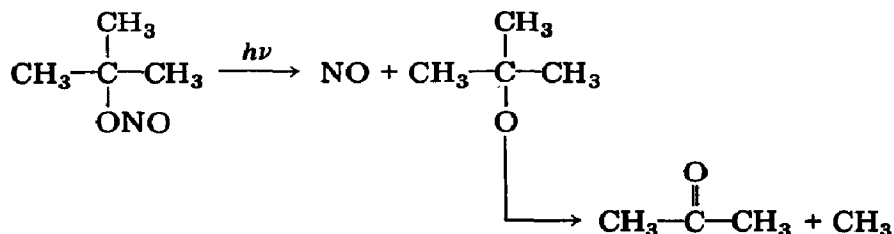
Low pressure photolysis of *tert*-butyl nitrite at 248 nm with an excimer laser includes secondary photolysis of products under conditions where these same products do not photolyze. The addition of HI to the photolyzing mixture suppresses secondary product formation.

## 1. Introduction

An experimental apparatus designed to investigate photolysis pathways has been built in our laboratory. A schematic diagram is shown in Fig. 1. The very low pressure photolysis (VLPΦ) technique [1] employed allows gas molecules to flow through a Knudsen cell at low pressures ( $10^{15}$  cm<sup>-3</sup> or less) where the average residence time is controlled by the rate of escape through an aperture [2]. The modulated molecular beam mass spectrometer analyzes the composition of the effluent gas; the Knudsen cell (or reactor) is fitted with high quality Suprasil windows to permit laser irradiation of the sample gas. The high sensitivity of the machine (*e.g.* the detection limit at unit mass resolution is about  $5 \times 10^{10}$  cm<sup>-3</sup>) enables good product detection. A Lambda Physics excimer laser was used to study the photolysis of *tert*-butyl nitrite at 248 nm where the photon energy is about 120 mJ pulse<sup>-1</sup>.

## 2. Results and discussion

*tert*-butyl nitrite (TBN) was chosen as a trial molecule to test the system because of its large cross section [3] at 248 nm and the relative stability of its photolysis products:



† Present address: Bell Laboratories, Murray Hill, NJ 07974, U.S.A.

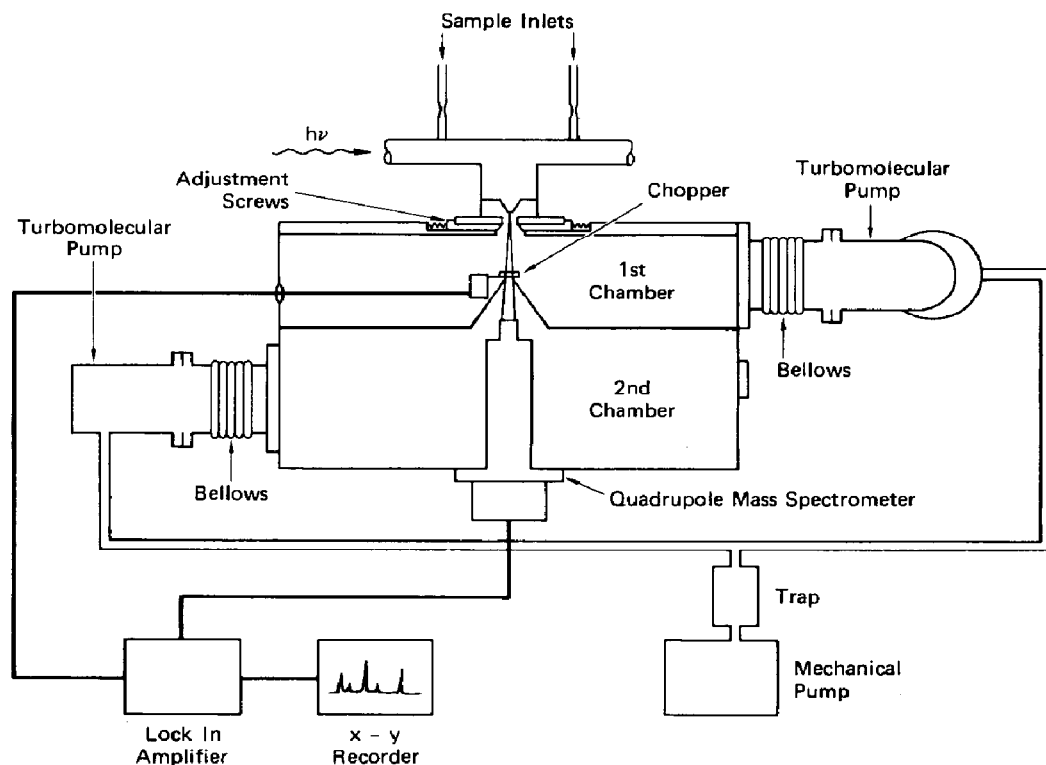


Fig. 1. Schematic diagram of VLP $\Phi$  apparatus.

The cell that was used has been characterized and described in the literature [1]. Prior to use, it was thoroughly cleaned and coated with Teflon (DuPont PTFE 852-200) according to specifications. The TBN (ICN Chemicals) was introduced into the cell at a concentration of about  $2 \times 10^{13} \text{ cm}^{-3}$  with an average residence time of 0.75 s. The sample was irradiated at 248 nm ( $120 \text{ mJ pulse}^{-1}$ ;  $50 \text{ pulses s}^{-1}$ ). A mass spectrum was recorded before and during photolysis; an example is given in Fig. 2. Care was taken to avoid hitting any surfaces other than the windows with the laser beam and to perform a blank photolysis run on the empty cell each day. TBN did not have a parent peak ( $m/e = 103$ ), so the cracking peak at  $m/e = 88$  served to monitor the concentration of unreacted TBN. Because an integrated mass spectrum was recorded, the  $50 \text{ pulse s}^{-1}$  laser repetition frequency was used to maintain a steady state concentration of photolysis products in the cell. Our experimentally measured absorption cross section for TBN compared favorably with the literature value [3] under these conditions. Mass balances were performed, and in the absence of any gas other than TBN the acetone yield ( $m/e = 58$ ) was 60% - 80% of the photodissociated TBN. Unfortunately, the mass spectrometer was equally sensitive to  $m/e = 30$  from the NO parent and the TBN cracking peak; thus no product information was ascertained at this mass.

A product peak at  $m/e = 28$  appeared, and if it was interpreted as CO formation its yield was 10% - 20% of the dissociated TBN. Some peak inten-

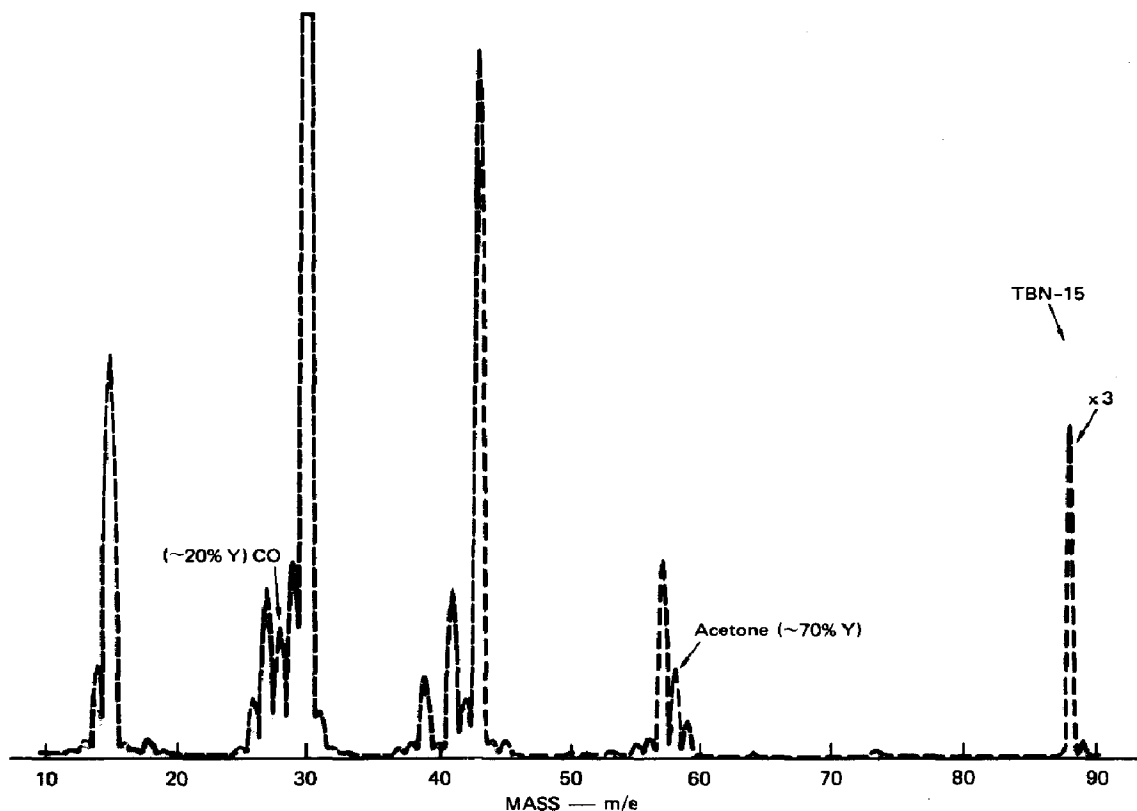


Fig. 2. Mass spectrum of TBN: —, unphotolyzed TBN; ---, TBN undergoing photolysis.

sity at  $m/e = 15$  was assigned to  $\text{CH}_3$  although no  $\text{CH}_4$  ( $m/e = 16$ ) was observed. At higher concentrations of TBN ( $10^{14} \text{ cm}^{-3}$  or more) the percentage photodissociated TBN decreased as a result of recombination competing with acetone formation from the *tert*-butoxy radical [4]. Also, *tert*-butanol ( $m/e = 58$ ) was formed as a product (about 10% yield) at the higher TBN pressures which was consistent with secondary reactions becoming important relative to acetone formation and/or secondary photolysis. However, the acetone yield was not improved over that from the lower pressure runs and no  $\text{CH}_4$  was measured.

In order to quantify the production of  $\text{CH}_3$ , HI was added to the cell in varying amounts and the concentration of  $\text{CH}_4$  was monitored. Several effects occurred during the photolysis of TBN in the presence of HI ( $2 \times 10^{14} - 2 \times 10^{15} \text{ cm}^{-3}$ ): (1) the acetone yield increased to about 100%, within experimental error, although the amount of photodissociated TBN did not change; (2) the peak at  $m/e = 28$  (CO) was no longer observed as a product; (3) the  $\text{CH}_4$  yield varied between 50% and 100%, giving about 100% yield only at high concentrations of HI ( $10^{15} \text{ cm}^{-3}$  or more). Many runs were performed to verify the reproducibility of these observations. Lower concentrations of HI that should have been more than adequate to trap  $\text{CH}_3$  [5] resulted in neither  $\text{CH}_4$  production nor increased acetone yield. Only at those

concentrations where gas-gas collisions became equal to or greater than gas-wall collisions were the above effects important. This suggested that perhaps the HI was acting primarily as a quencher rather than as a titrant. Under our conditions, the *tert*-butoxy radical could have an excess energy of as much as 60 kcal mol<sup>-1</sup> which may have been sufficient to access the first excited electronic state of the radical. Two different experiments were performed, one in which O<sub>2</sub> was substituted for HI and the other in which CH<sub>4</sub> was used instead of HI; in both cases the acetone yield resembled that of the pure TBN experiments although the *m/e* = 28 (CO) production was not significant. These data may indicate that an excited electronic state is not involved as the addition of relatively efficient electronic quenchers such as O<sub>2</sub> and CH<sub>4</sub> should have increased the acetone yield. Perhaps HI is a much more efficient quencher.

To check for complications from absorption of products by the Teflon-coated surface (which could have been reduced by monolayers of HI), the Teflon was completely removed and the photolysis of TBN was repeated in the Pyrex cell. The acetone yield still remained at about 70%. Although this test did not absolutely rule out product loss on the walls, it is rather unlikely to have been a significant process and remain unchanged by the absence of the Teflon surface.

Reaction of the methyl radical with the excited *tert*-butoxy radical seemed inconsistent with the facts that no CH<sub>4</sub> was observed except with HI addition and that several lower TBN pressure runs (about 10<sup>12</sup> cm<sup>-3</sup>) did not increase the acetone yield. Secondary photolysis could certainly have been a complicating process in this study, given that the *m/e* = 28 peak, if interpreted as CO, nearly compensated for the incomplete acetone yield and that this peak disappeared when the acetone yield increased to about 100% with HI present. Several runs were made in which acetone was introduced into the Teflon-coated cell (about 10<sup>13</sup> cm<sup>-3</sup>) and was photolyzed under the same conditions as TBN; there were no changes in the mass spectra nor was there any apparent dissociation (*m/e* = 58). The laser repetition frequency was reduced to 10 Hz and the TBN spectra were again recorded. Clearly a single-shot experiment with real-time product analysis would have been the ideal test for secondary photolysis, but the above experiment permitted the same steady state product analysis with a reduced photon flux in the same experimental configuration. The negative results do not rule out the importance of secondary photolysis since several laser shots may have been adequate to produce our observations. It does seem unusual that HI addition [6] should have reduced this process, especially in view of the many wall collisions that occurred in the pure TBN experiments. However, the conclusion that secondary photolysis took place is consistent with much of the experimental data.

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