

# Formation of Nitrogenous Compounds in the Photooxidation of *n*-Butane under Atmospheric Conditions

Efthalia Evmorfopoulou and Sotirios Glavas\*

University of Patras, Department of Chemistry, EL-26500 Patras, Hellas

**Summary.** The photooxidation of *n*-butane under atmospheric conditions in the presence of NO<sub>x</sub> resulted in the formation of the following nitrogenous products: peroxy acetyl nitrate 23, *sec*-butyl nitrate 16, *n*-butyl nitrate 1.3, ethyl nitrate 1.3, peroxy *n*-butyryl nitrate 1.3, and peroxy propionyl nitrate 0.5% of the initially added odd nitrogen. In addition, an electron capturing compound eluting at the retention time of *sec*-propyl nitrate was also observed accounting for 5% of initial NO<sub>x</sub>. Butan-2-one was the major product of conversion of *n*-butane with a yield of 37%. From product ratios it is evident that the formation of *sec*-butyl nitrate is favored over that of *n*-butyl nitrate by a factor of 2.1. The rate of reaction of *sec*-butoxy radicals with oxygen is equal to their decomposition rate.

**Keywords.** *n*-Butane; Photooxidation; Product yield; PAN; PPN; PnBN; Alkyl nitrates.

## Zur Bildung von Stickstoffverbindungen bei der Photooxidation von *n*-Butan unter atmosphärischen Bedingungen

**Zusammenfassung.** Die Photooxidation von *n*-Butan unter atmosphärischen Bedingungen und in Gegenwart von NO<sub>x</sub> führt zur Bildung folgender stickstoffhaltiger Verbindungen: Peroxyacetylnitrat 23, *sec*-Butylnitrat 1.3, Ethylnitrat 1.3, Peroxy-*n*-butyrylnitrat 1.3 und Peroxypropionylnitrat 0.5% des zugesetzten NO<sub>x</sub>. Zusätzlich wurde eine elektronenaffine Verbindung mit der Retentionszeit des *sec*-Propylnitrats im Ausmaß von 5% bezogen auf NO<sub>x</sub> gefunden. Butanon-2 war mit einer Ausbeute von 37% das Hauptprodukt. Aus den Produktverhältnissen folgt, daß die Bildung von *sec*-Butylnitrat gegenüber der von *n*-Butylnitrat um einem Faktor 2.1 bevorzugt wird. Darüber hinaus wurde gefunden, daß die Reaktionsrate der *sec*-Butoxyradikale mit Sauerstoff gleich der Rate der Zersetzung der *sec*-Butoxyradikale ist.

## Introduction

The development of control strategies for the abatement of formation of photooxidants, mostly ozone, in urban areas is usually carried out with the application of an appropriate air quality model. A significant component of such a model deals

\* Corresponding author

with the chemical transformation of ozone precursor emissions. The validation of the chemical mechanisms of air pollution is usually performed utilizing smog chamber data which can be obtained with hydrocarbon mixtures [1, 2, 3] or single hydrocarbons [4, 5, 6].

*n*-Butane is a significant component of urban [7] and rural [8] ambient air hydrocarbons; in addition, it may serve as a surrogate of the saturated hydrocarbons of the atmosphere in the photochemical mechanisms [2]. Although the photooxidation mechanism of *n*-butane is rather well established, the nitrogen mass balance is rather low [4]. The speciation of nitrogenous products is very important because inactivation of  $\text{NO}_x$  ( $=\text{NO} + \text{NO}_2$ ) into compounds which remove  $\text{NO}_x$  from the ozone formation cycle would result in less ozone formation. The nitrogenous compounds which serve as sinks of  $\text{NO}_x$  are peroxy acyl nitrates (may be considered as temporary sinks because of their thermal instability), alkyl nitrates, and nitric acid. Three of the past studies of *n*-butane reported alkyl nitrate yields [4, 9, 10], two reported yields of peroxy acetyl nitrate (*PAN*) [4, 11], and one quantified the formation of nitric acid [11]. In addition to the products reported in past studies, two further peroxy acyl nitrates, peroxy *n*-butyryl nitrate (*PnBN*) and peroxy propionyl nitrate (*PPN*), would be expected to be formed within the currently acceptable mechanism of *n*-butane photooxidation. However, although their precursor aldehydes, *n*-butanal and *n*-propanal, have been experimentally measured [4, 5], *PnBN* and *PPN* were not reported.

In the present work, we have quantified all the previously measured alkyl nitrates. We report a previously not measured alkyl nitrate. In addition, we determined *PnBN* and *PPN*. We also measured butanone, the major product of transformation of *n*-butane, under atmospheric conditions. From the measured product ratios we derive rate constant ratios important for the formation of alkyl nitrates as well as to the decay steps of butoxy radicals.

## Results and Discussion

Two sets of experiments were carried out with six experiments in each set. In the first set the reactants were butane/ $\text{NO}/\text{NO}_2$ , in the second one butane/ $\text{NO}_2$ . The total irradiation time was six hours. Within this time,  $\sim 10\%$  of butane reacted when  $\text{NO}$  was present and  $\sim 20\%$  when  $\text{NO}$  was absent. Reactant concentrations and product yields are given in Table 1. The main product was butanone; the nitrogenous products in descending order of yield were: *PAN*, *sec*-butyl nitrate, a compound eluting at the retention time of *sec*-propyl nitrate, *PnBN*, ethyl nitrate, *n*-butyl nitrate, and *PPN*. *PPN* was observed only in the experiments carried out with  $\text{NO}_2$  alone. Although the concentration of formed butanone was significantly higher in the experiments without initial  $\text{NO}$ , the resulting yields were the same due to the larger consumption of *n*-butane. The remaining products were formed in similar amounts in both sets, but their yields were significantly different. The stated uncertainty is  $\pm$  one standard deviation.

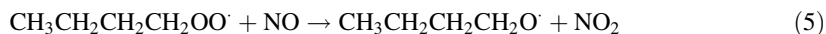
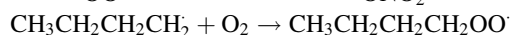
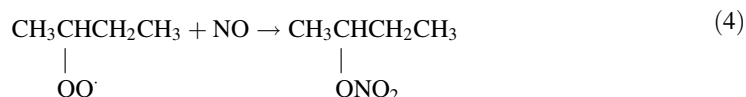
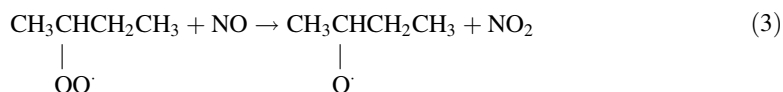
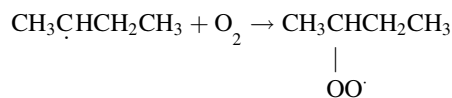
The only route of ambient air alkane degradation is *via* their reaction with hydroxyl radicals. This occurs through H-atom abstraction: 85% from a secondary and 15% from a primary H-atom [12]. The formed alkyl radical will add quickly to an oxygen molecule, forming the respective alkyl peroxy radical. In the presence of

**Table 1.** Reactant concentrations<sup>a</sup> and product yields of *n*-butane photooxidation in the presence of NO<sub>x</sub>

<i>n</i> -Butane	NO <sub>2</sub>	NO	PAN	<i>PmBN</i>	<i>PPN</i>	<i>sec</i> -butyl nitrate	<i>n</i> -butyl nitrate	<i>sec</i> -propyl nitrate <sup>b</sup>	Ethyl nitrate	Butanone
Set 1:	3100±13	107±3	0	0.002± 1×10 <sup>-4</sup>	8×10 <sup>-4</sup> ± 6×10 <sup>-5</sup>	2.7×10 <sup>-2</sup> ± 2×10 <sup>-4</sup>	2.3×10 <sup>-3</sup> ± 6×10 <sup>-4</sup>	7.2×10 <sup>-3</sup> ± 4×10 <sup>-4</sup>	0.003±1×10 <sup>-4</sup>	0.37±0.01
Set 2:	3080±42	54±5	0.07±0.01	0.004± 1×10 <sup>-3</sup>	0	5.3×10 <sup>-2</sup> ± 8×10 <sup>-3</sup>	4.3×10 <sup>-3</sup> ± 6×10 <sup>-4</sup>	1.8×10 <sup>-2</sup> ± 3×10 <sup>-3</sup>	0.008±1×10 <sup>-3</sup>	0.37±0.02

<sup>a</sup> Reactant concentrations in ppbv (1 ppbv = 2.5×10<sup>10</sup> molecules/cm<sup>3</sup> at 1 atm and 298 K); <sup>b</sup> see text

nitrogen monoxide, the alkyl peroxy radicals will react with NO and will either oxidize NO to NO<sub>2</sub> or will form the respective alkyl nitrate, as shown in Scheme 1.



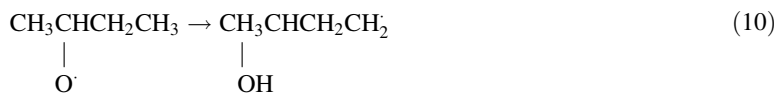
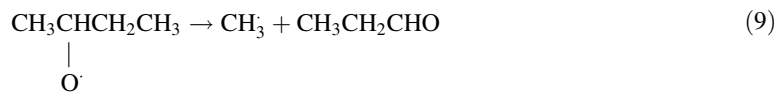
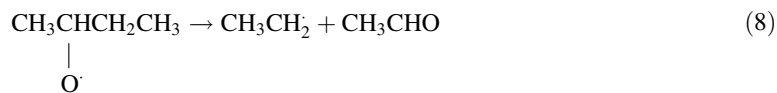
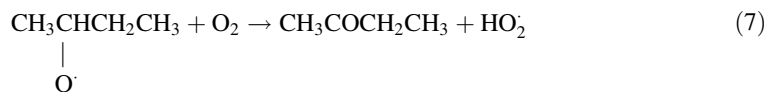
Scheme 1

### Secondary alkyl nitrate versus primary alkyl nitrate

The ratio of concentrations of *sec*-butyl nitrate to *n*-butyl nitrate, obtained from Table 1, is 11.7 for set 1 and 12.3 for set 2. These values are slightly lower than the 14.3 value previously reported [9]. Ignoring the rate of destruction of the alkyl nitrate products by the hydroxyl radicals, the ratio of formed butyl nitrates is [*sec*-butyl nitrate]/[*n*-butyl nitrate] = (( $k_4/(k_3+k_4)$ )/( $k_6/(k_5+k_6)$ )) ·  $f_1/f_2$ , where  $k_i$  are the rate constants of the reactions shown in Scheme 1 and  $f_1$  and  $f_2$  are 0.85 and 0.15, respectively. The correction of the products due to their reaction with hydroxyl radicals [13, 14], carried out according to *Atkinson et al.* [9], amounted to only a few percent; thus, no correction was applied. Substitution yields ( $k_4/(k_3+k_4)$ )/( $k_6/(k_5+k_6)$ ) = 2.1 for data set 1 and (( $k_4/(k_3+k_4)$ )/( $k_6/(k_5+k_6)$ )) = 2.2 for data set 2. These values indicate that the formation of the secondary alkyl nitrate is favored over that of the primary nitrate by a factor of 2.1–2.2, in agreement with the value of 2.5 reported by *Atkinson* [15] for all secondary and primary nitrates as derived from comparisons of experimental values of rate constant ratios of secondary alkyl nitrate formation over the total reaction of the secondary alkyl peroxy radicals with the respective values for the formation of primary alkyl nitrates [12].

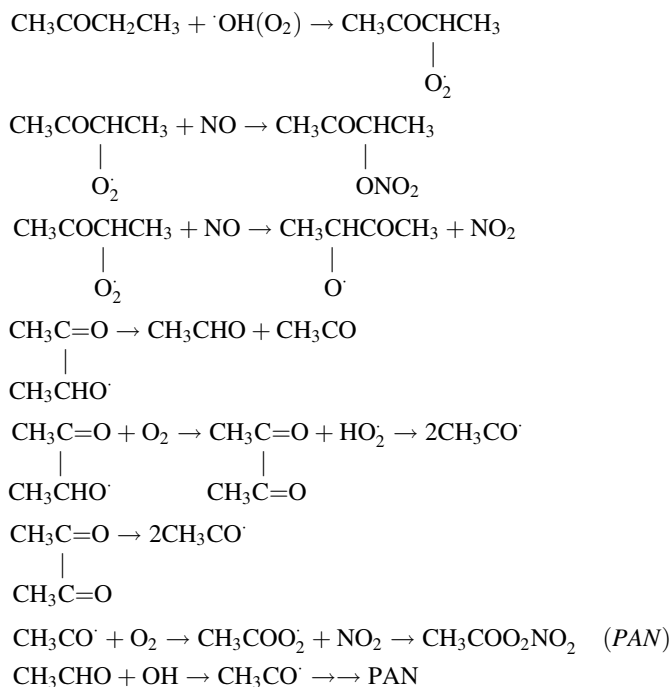
### Transformation of *sec*-butoxy radicals

The *sec*-butoxy radicals formed in reactions (3) and (5) may react with oxygen, decompose, or isomerize either by 1,4 or 1,5 H-shift. In the case of the *sec*-butoxy radicals, the above steps are shown in Scheme 2.



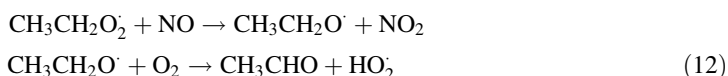
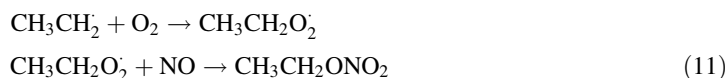
Scheme 2

Reaction (7) leads to butanone, the most abundant product of the photooxidation of *n*-butane under atmospheric conditions. The obtained yield for all data was  $0.37 \pm 0.02$ . This is similar to the 0.40 value obtained by *Cox et al.* [5], but significantly larger than the 0.06 value of *Carter et al.* [4]. Butanone can react with OH radicals by H-atom abstraction from the secondary hydrogens, eventually leading to PAN. Biacetyl may or may not be formed according to Scheme 3 as proposed by *Cox et al.* [5].



Scheme 3

Reaction (8) leads to acetaldehyde which may form *PAN* according to the above scheme and ethyl radicals which may form ethyl nitrate according to Scheme 4.



#### Scheme 4

Reaction (9), also a decomposition like reaction (8), leads to methyl radicals which – following the analogous reaction scheme of ethyl radicals-lead almost exclusively to formaldehyde, as formation of methyl nitrate is less favorable because of the small size of the nitrate [16]. The formed *n*-propanal may, in analogy to acetaldehyde, yield *PPN*. Although *n*-propanal has been observed in past studies of *n*-butane [4, 5], *PPN* was not reported. *PPN* has been measured in ambient air [17]. Thermochemical calculations have shown that decomposition by reaction (8) is favored over reaction (9) by a factor of 160 [15]. Thus, all products from reaction (9) will be negligible, and therefore contribution of this step to the formation of *PPN* would also be negligible.

The 1,4 H-shift isomerization reaction (10) leads to the formation of hydroxy alkyl radicals which would be expected to react similarly to alkyl radicals, although at different rates. No product was detected from this path. Thermochemical calculations have shown that a 1,4 H-shift is not favorable; the estimated rate constant is  $26 \text{ s}^{-1}$  [13]. Thus, the dominating steps would be reactions (7) and (8).

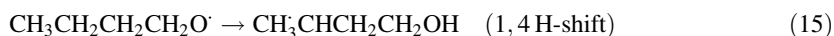
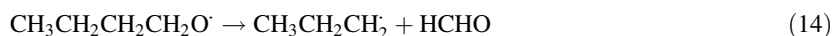
According to the above reaction schemes, the ratio of formed ethyl nitrate to butanone would be equal to  $[\text{Ethyl nitrate}]/[\text{Butanone}] = (k_8/(k_7[\text{O}_2])) \cdot k_{11}/(k_{11}+k_{12})$ . The rate constant ratio  $k_{11}/(k_{11}+k_{12})$  was experimentally determined to be 0.014 [9] and was calculated to be 0.01 [16]. Substitution of the value 0.008 (first set of data) yields  $k_8/k_7 = 2.9 \times 10^{18} \text{ molecules/cm}^3$  and of 0.02 (second set of data)  $8.1 \times 10^{18} \text{ molecules/cm}^3$ . These rate constant ratios are comparable to the experimentally obtained ratios of  $3.1 \times 10^{18}$  [4] and  $2.6 \times 10^{18} \text{ molecules/cm}^3$  [5], but are significantly larger than the  $2.6 \times 10^{16} \text{ molecules/cm}^3$  reported by *Heiss et al.* [18] and 5–10 times larger than the thermochemically estimated ratio of  $6 \times 10^{17}$ . The thermochemical calculations, however, have an inherent uncertainty of a factor of 5 [15]. Substitution of the  $k_7$  value of  $7.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{s}^{-1}$  [13] yields  $k_8 = (2.5\text{--}5.3) \times 10^4 \text{ s}^{-1}$ , a value larger by an order of magnitude than the thermochemically calculated value [15]. Taking the mean value of the two sets of  $k_8$  we deduce that reactions (7) and (8) occur in a ratio of 50:50. This result along with the later derived  $k_4/k_3$  ratio results in a yield of butanone of 0.40 which is in excellent agreement with the experimental value given earlier.

The ratio of formed *sec*-butyl nitrate to butanone yields  $[\textit{sec}\text{-Butyl nitrate}]/[\text{Butanone}] = k_4/(k_3 \cdot f_7)$ . Substitution of the experimental values of set 1 yields  $k_4/k_3 = 0.04$ , those of set 2  $k_4/k_3 = 0.07$ . The value of 0.093 calculated by the fall-off expression of Carter and Atkinson [16] is similar to our derived values. The rate constant ratio of 0.04–0.07 indicates that the yield of *sec*-butyl nitrate would be 0.03–0.06. As derived earlier, the formation of secondary alkyl nitrates is favored

over the primary ones by a factor of 2.1. Therefore, the total butyl nitrate yield in our system would be 0.05–0.09, in agreement with the previous value of 0.077 [9].

#### *Transformation of n-butoxy radicals*

The *n*-butoxy radicals formed from reaction (5) may also react with oxygen, decompose, and isomerize according to Scheme 5.



#### Scheme 5

The *n*-butanal formed in reaction (13) was observed in the smog chamber study of *Carter et al.* [4]. *n*-Butanal would be expected to react with hydroxyl radicals or photolyze (the photolysis rate constant is unknown) to yield peroxy *n*-butyryl nitrate, similarly to the reaction sequence giving *PAN* from acetaldehyde. *PnBN*, however, like *PPN* was not observed in the previous smog chamber study of *n*-butane [4]. As far as we know, *PnBN* has never been reported in smog chamber studies, although it has been measured in ambient air [17]. *PnBN* was observed in the products with a 2.5 times higher yield than that of *PPN*.

The decomposition reaction (14) yields *n*-propyl radicals and formaldehyde. The *n*-propyl radicals would be expected to react, as shown earlier for ethyl radicals, to yield *n*-propyl nitrate and *n*-propanal, part of which may be converted to *PPN*. However, *n*-propyl nitrate was not observed in the products. The only three carbon alkyl nitrate observed was that eluting at the retention time of *sec*-propyl nitrate, whose formation, however, cannot be explained with above reaction schemes. *PPN* was observed only in the experiments in which the reactants did not include NO. The presence of NO would destroy *PPN* through destruction of peroxy propionyl radicals as was shown to be the case with other similar peroxy acyl radicals [19, 20]. Thus, the small *PPN* precursor sources shown earlier to be negligible for *sec*-butoxy radicals and those obtained from reaction (14), along with the destruction of *PPN* by NO and possibly its coelution with *sec*-butyl nitrate, a difficulty which we have overcome with the use of high resolving power capillary chromatography, are probably the reasons why *PPN* was not reported in past photooxidation studies of *n*-butane.

If we ignore the formation of *n*-propyl nitrate, which anyway according to the fall-off expression of *Carter and Atkinson* [16] accounts for 5% of the conversion of *n*-propyl peroxy radicals with NO, and assume that the rates of formation of *PnBN* from *n*-butanal and *PPN* from *n*-propyl radicals are the same, the product ratio  $[\text{PnBN}]/[\text{PPN}] = k_{13}[\text{O}_2]/k_{14}$  yields  $k_{14}/k_{13} = 2.0 \times 10^{18}$  molecules/cm<sup>3</sup>. Substitution of the  $k_{13}$  value  $8 \times 10^{-15}$  cm<sup>3</sup>molecule<sup>-1</sup> · s<sup>-1</sup> [15] yields  $k_{14} = 1.6 \times 10^4$  s<sup>-1</sup>, a value 670 times larger than the thermochemically calculated one [15]. This difference, although it may be reduced by an order of magnitude due to the uncertainty in the thermochemical calculations, is still too large to be accounted

for. No products were observed that could be attributed to the isomerization reactions (15) and (16). Thermochemical calculations have shown, however, that 1,5 H-shift dominates over the 1,4 H-shift [15]. Thus, reactions (13) and (16) would be most important.

At the end of the irradiation period, the sum of nitrogenous products of Table 1 accounts for 46–50% of the initially added odd nitrogen in both sets of experiments. In addition at the end of each run on the average 30.4 ppb  $\text{NO}_x$  (mostly  $\text{NO}_2$ , but also HONO and traces of NO) were left. Thus, the nitrogen mass balance in these experiments was 74–78%. If we add to the above concentrations of nitrogenous species the nitric acid concentration of 24 ppb, determined in experiments carried out under the same conditions and with similar initial reactant concentrations [11], the nitrogen mass balance makes up to 97–101% of the initially added odd nitrogen, indicating that all significant nitrogenous products have been accounted for.

## Experimental

All experiments were carried out in 200 A FEP teflon chambers of ~600 liters volume equipped with a miniature teflon coated fan. The Teflon bags were housed in an aluminum box and were photolyzed by a mixture of Philips lamps with maximum emissions of 310 and 365 nm. The temperature was maintained at  $25 \pm 2^\circ\text{C}$  by a commercial air conditioner.

Ambient air was purified by an Aadco air purification system, supplied with a methane reactor so that the sum of hydrocarbons contained in the purified air was less than 10 parts per billion ( $1:10^9$ ) carbon. The relative humidity of the dried purified air was adjusted to 30–40% by passing part of the bag filling air through pure distilled water. Photolysis of purified air for six hours formed 5 ppb ozone and zero PAN.  $\text{NO}_2$  was prepared daily in darkened glass flasks by oxidation of 99.85% nitrogen monoxide, obtained from Messer Griesheim, with a large excess of medical grade oxygen, obtained from Linde Hellas. *n*-Butane, 99% minimum stated purity, was obtained from Messer Griesheim and was used without further purification. GC/FID analysis of *n*-butane showed only one peak. PAN, PPN, and PnBN were prepared by nitration of the respective peracids [21]. The alkyl nitrates were prepared in the dark by addition of 1-propyl, 2-propyl, 1-butyl, and 2-butyl bromides obtained from Aldrich to a saturated solution of  $\text{AgNO}_3$  in  $\text{CH}_3\text{CN}$  at room temperature. NO and  $\text{NO}_x$  were determined by the ozone chemiluminescence method. The catalyst used to convert  $\text{NO}_x$  into NO was  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . In separate experiments it was determined that this catalyst converts  $\text{NO}_2$ , peroxy acyl nitrates, and alkyl nitrates into NO but does not convert nitric acid.

PAN, PPN, PnBN, and the alkyl nitrates were initially separated on a 5 m HP-1 non polar 100% methyl silicone gum column of 0.53 mm i.d. and were detected by GC/ECD. Because PAN coeluted with 2-propyl nitrate and PPN with *sec*-butyl nitrate, quantification of these compounds was carried out by heating the ECD, in separate duplicate experiments, at  $150^\circ\text{C}$ , a temperature at which we determined that the peroxyacyl nitrates are thermally destroyed and not detected by the ECD, whereas the alkyl nitrates are not affected. We thus found that on the average 95% of the peak of PAN and *sec*-propyl nitrate was due to PAN, whereas only 10% of the PPN and *sec*-butyl nitrate peak was due to PPN. In later experiments, the 5 m 0.53 mm i.d. column was replaced by a HP-1 15 m 0.32 mm i.d. one. As has been also shown previously [22], the longer and smaller diameter column separated well the PPN from the *sec*-butyl nitrate and PAN from *sec*-propyl nitrate. The results from the 0.53 mm column, after correction with the heated detector experiments, were similar to those of the 0.32 mm column. The calibration of the ECD for the peroxy acyl nitrates was carried out after their alkaline hydrolysis and determination of the formed  $\text{NO}_2^-$  using Dionex ion chromatography [23]. *n*-Butane and butanone were analyzed by GC/FID using a HP-1 10 m 0.53 mm i.d. column.



Two Hewlett-Packard 5890 gas chromatographs were used. Reactants and products were directly injected to GC using Precision Sampling gas tight syringes.

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