Optimization of the photochemical generation of trifluoronitromethane, CF_3NO_2, and a refined purification technique☆

John O. Hauptfleisch, Matthew D. Hennek, Alfred Waterfeld, Richard E. Fernandez, Joseph S. Thrasher *

Department of Chemistry, The University of Alabama, 250 Hackberry Lane, Tuscaloosa, AL 35487, USA

ABSTRACT

The gas-phase photochemical generation of CF_3NO_2 from CF_3I and NO_2 was found to be equilibrium limited. The formation of CF_3NO_2 is favored at low pressure and high temperature, where the concentration of the reactive species $^\bullet NO_2$ is the greatest, and unfavored at high pressure and low temperature, where the concentration of N_2O_4 is greatest. The results from varying the stoichiometric ratio of reactants, pressure, temperature, and reaction time in an attempted scale-up of this reaction are consistent with the reaction being equilibrium limited. The best reaction conditions allowed the generation of only 1–3 g of CF_3NO_2 per batch reaction in an approximate 16-L vessel. As long as reaction conditions are chosen so that all of the starting CF_3I is consumed, caustic scrubbing affords a significantly faster, less expensive, and more practical purification method than those previously published.

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1. Introduction

Trifluoronitromethane, CF_3NO_2, has been a characterized compound for over 50 years. Many different methods have been reported for synthesizing it, including (1) oxidation of trifluoronitrosomethane, CF_3NO [1–9], (2) thermal generation using trifluoroacetic acid [10–12], (3) thermal decomposition of $CF_3N(O)NCF_3$, acyl nitrates, and molecules formed from reactions with fluorine nitrate [13,14], and (4) unique methods [4,15–17]. Until recently, no efficient one-step method for generating CF_3NO_2 existed. However, in 2002 Lu and Thrasher found the first effective one-step method for generating CF_3NO_2 from CF_3I and NO_2 using a diazo (superblue) light source ($\lambda_{max} = 420$ nm). At the time, the reaction conditions were not optimized, and only ca. 0.5 g batches of CF_3NO_2 were synthesized. In addition, the purification method was both time-consuming and relatively expensive, requiring both CsF and AlF₃ to remove the byproducts of the reaction [18]. Subsequently, Shreeve et al. discovered a one-step method utilizing Umemoto's reagent for the electrophilic trifluoromethylation of sodium nitrite, NaNO₂. They achieved excellent yields of CF_3NO_2 (∼90%), and purification of the product from the reaction mixture was quick and efficient [19]. However, the high cost of Umemoto's reagent, ca. \$80/g (Sigma–Aldrich – 2011), makes this method uneconomical for preparing very large quantities of CF_3NO_2.

Because the reaction conditions for the method of preparing CF_3NO_2 by Lu and Thrasher were not optimized, e.g., no details were given on the effect of the stoichiometric ratio of the starting materials, pressure, temperature, or reaction time, it was felt that this reaction warranted further study. A series of experiments were carried out testing these variables in an effort to increase both the percent yield as well as the scale of the reaction. Furthermore, a new, more efficient method for the purification of CF_3NO_2 resulting from this photochemical reaction was developed that reduces both the cost and time of purification as well as increases the amount of material that can be purified in a single batch.
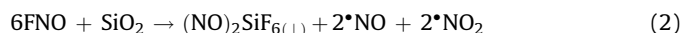
2. Results and discussion

2.1. Synthesis

The experiments within this paper are a continuation of the Lu and Thrasher study [18]. A diazo blue lamp ($\lambda_{max} = 420$ nm) photoreactor (16.3-L) is used to facilitate the reaction of CF_3I and $^\bullet NO_2$ as shown in Eq. (1).

$$2CF_3I + 2^\bullet NO_2 (\text{excess}) \rightarrow CF_3NO_2 + COF_2 + FNO + I_2 \quad (1)$$
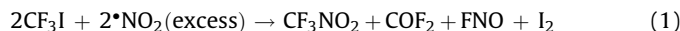
The FNO molecule is highly reactive and will interact with the glass of the reaction vessel forming a semi-transparent white solid as show in Eq. (2) [20]. This process typically removes 0.1–0.5 g of mass from the reaction vessel each run, and this loss should be monitored for obvious safety reasons.

$$6FNO + SiO_2 \rightarrow (NO)_2SiF_{6(\downarrow)} + 2^\bullet NO + 2^\bullet NO_2 \quad (2)$$

$$^\bullet NO + ^\bullet NO_2 \leftrightarrows N_2O_3 \quad (3)$$

Various conditions of the reaction were investigated including (1) the stoichiometric ratio of $^\bullet NO_2$:CF_3I (ranging from 0.4 to 5.2:1), (2) pressure (0.1–0.5 atm absolute), (3) temperature (10–55 °C), and (4) reaction time (4–16 h, although many reactions where time was not varied were run for 18 h). The results of these experiments were monitored by ^{19}F NMR spectroscopy by comparing the mole ratio of CF_3NO_2:CF_3I. A calculation for mol% CF_3NO_2 was made using Eq. (4).

$$CF_3NO_2 \; mol\% = \frac{\text{Integrated intensity of } CF_3NO_2}{(\text{Integrated intensity of } CF_3NO_2 + \text{Integrated intensity of } CF_3I)} \times 100 \tag{4}$$

In order to avoid any issues with differences in the partial pressures of CF_3NO_2 and CF_3I that might otherwise skew the results, entire reaction masses were always kept in the gaseous state. The NMR measurements were taken on samples after minimal purification, i.e., a trap-to-trap distillation to remove the majority of the unreacted $^\bullet NO_2$, but prior to the caustic wash. This eliminates possible errors in the mol% of CF_3NO_2 from the 1% to 5% loss in the mass of CF_3I during the caustic wash.

2.1.1. Effect of stoichiometric ratio of reactants on generation of CF_3NO_2

Varying the stoichiometric ratio of the starting materials was investigated for several reasons. First, a convergence of the stoichiometric ratios of CF_3I:$^\bullet NO_2$ would help minimize the purification process, and second, more CF_3NO_2 can be produced per batch (*vide infra*). Table 1 summarizes the experiments where CF_3I is the limiting reagent in Reactions #2–#4 and $^\bullet NO_2$ is the limiting reagent in Reaction #1, with the simplifying assumption of $^\bullet NO_2$ being 100% of the equilibrium composition with its partner N_2O_4. Obviously, this does not reflect reality but greatly simplifies the comparison of one reaction to another, especially since $^\bullet NO_2$ is being consumed during each reaction and thus the equilibrium is constantly being shifted via Le Chatlier's principle. This oversimplification also makes sense when thinking about whether or not $^\bullet NO_2$ is truly the limiting reagent, especially in reactions that result in high mol% of CF_3NO_2. The total pressure at ambient temperature for the reactions was 0.3 atm (again, hypothetical 100% $^\bullet NO_2$ basis), the reaction time was limited to 18 h, and the reaction vessel temperature due to heating from the lamp, was between 45 and 50 °C.

Under the reaction conditions, the lowest stoichiometric excess of $^\bullet NO_2$:CF_3I produces the highest mol% of CF_3NO_2. As the deviation in the stoichiometric ratio increases, the mol% CF_3NO_2 decreases significantly. These results suggest that the partial pressure of $^\bullet NO_2$ in the system has a significant effect on the final composition of the mixture. When CF_3I is the limiting reagent, the partial pressure of $^\bullet NO_2$ is at its highest point when the stoichiometric ratio of reactants is the closest to 1:1, i.e., the well-documented equilibrium of 2 $^\bullet NO_2 \leftrightarrows N_2O_4$ favors the reactive $^\bullet NO_2$ species [21]. For the larger stoichiometric ratios, 1:3 and 1:5, a similar equilibrium has been established between $^\bullet NO_2/N_2O_4$, and little difference in the

final mol% of CF_3NO_2 is observed under these conditions. Thus, having a stoichiometric ratio of NO_2:CF_3I greater than 3:1 is not practical for this experiment. If other variables are changed, such as the temperature or pressure, a deviation in the final mol% of CF_3NO_2 in Reactions #3 and #4 will occur.

When $^\bullet NO_2$ is the limiting reagent, a number of different fluorinated products are formed, most of which were not identified. The majority (94%) of the mixture is still CF_3I and CF_3NO_2, but hexafluoroethane, C_2F_6 (^{19}F NMR spectrum, $\delta = -89.0$ ppm), is now generated and consists of ~5% of the total reaction mixture. Statistically, the excess $^\bullet CF_3$ radicals now have much more of an opportunity to react with one another, which does not occur to any measurable extent when an excess of $^\bullet NO_2$ is present.

2.1.2. Effect of pressure on the generation of CF_3NO_2

In order to maximize the yield of the photochemical reaction, one could approach, but not exceed, the safe operating, maximum pressure of the Pyrex® vessel. It was quickly discovered that scaling up this reaction by increasing the pressure was ineffective. Once the pressure of reactants in the vessel was raised above 0.5 atm, the conversion to CF_3NO_2 was close to 0 mol%. The reactions studied varied in total pressure from 0.1 to 0.5 atm (calculated at ambient temperature and based on the simplifying assumption of $^\bullet NO_2$ being 100% of the equilibrium composition with its partner N_2O_4) with a reaction time of 18 h and a stoichiometric ratio of 3: 1 ($^\bullet NO_2$:CF_3I, see Table 2).

Similar to the experiments with varying stoichiometric ratios, the driving force for the success of this photochemical reaction is the equilibrium of 2 $^\bullet NO_2 \leftrightarrows N_2O_4$. As the pressure in the system is increased, the partial pressure of the N_2O_4 molecules increases [cf. 21]. The shift in the equilibrium towards the less reactive N_2O_4 species results in a drop in the mol% of CF_3NO_2 produced. Unless the temperature is raised significantly above the maximum of our reaction chamber (60–65 °C), the conversion to CF_3NO_2 will decrease significantly.

2.1.3. Effect of temperature on the generation of CF_3NO_2

Along with pressure, temperature has the most significant effect on the 2 $^\bullet NO_2 \leftrightarrows N_2O_4$ equilibrium. As the temperature is increased, the equilibrium is shifted towards the reactive $^\bullet NO_2$ molecules, while N_2O_4 is the dominant species as the temperature is decreased. Bauer has summarized in a review the relations of both temperature and pressure in the 2 $^\bullet NO_2 \leftrightarrows N_2O_4$ equilibrium [21]. Variations in the reaction temperature were difficult to study in the current photochemical reactor set-up. Heat can be removed from the system fairly easily by turning on a fan built into the system. This normally kept the system between 40 and 45 °C. In order to achieve the lowest reaction temperatures, ca. 10 °C, the

Table 1
Stoichiometric ratios of $^\bullet NO_2$:CF_3I.

Reaction #	Mol ratio of $^\bullet NO_2$:CF_3I[a]	Mol% CF_3NO_2
#1	0.4:1.0	28%[b]
#2	1.1:1.0	76%
#3	3.0:1.0	49%
#4	5.0:1.0	53%

[a] Hypothetical 100% $^\bullet NO_2$ basis.
[b] Conversion limited.

Table 2
Pressure effects on the photochemical generation of CF_3NO_2.

Reaction #	Pressure (atm)[a]	Mol% CF_3NO_2
#5	0.1	99%
#6	0.2	79%
#7	0.3	49%
#8	0.4	37%
#9	0.5	29%

[a] Hypothetical 100% $^\bullet NO_2$ basis.

Table 3
Temperature of reaction at various pressures and stoichiometric ratios.

Reaction #	CF_3I:$^\bullet NO_2$[a]	Pressure (atm)[a]	Temp. (°C)	Mol% CF_3NO_2
#10	1:5.05	0.44	52.0	83%
#11	1:3.22	0.30	50.0	100%
#12	1:3.27	0.16	55.0	100%
#13	1:1.56	0.14	49.3	100%
#14	1:4.87	0.30	12.2	31%
#15	1:5.21	0.30	11.7	27%
#16	1:1.07	0.30	12.0	31%
#17	1:1.01	0.30	10.5	34%

[a] Hypothetical 100% $^\bullet NO_2$ basis.

entire chamber was placed in a walk-in cold room set at 0 °C. Adding heat to the system was more problematic as the light fixtures used had a tendency to fail at temperatures above 75 °C. Thus, insulating the system to trap more heat and achieve a higher reaction temperature was impractical. Heating the reaction vessel directly with either a heat tape or a heat gun would also have been ineffective due to either blockage of light or space restraints on the reaction chamber. Thus, the maximum achievable temperature in the current reaction chamber was between 55 and 60 °C.

Table 3 shows a collection of data with varying stoichiometric ratios, pressures, and temperatures but at a constant reaction time of 18 h. The results clearly indicate that the reaction is equilibrium limited (2 $^\bullet NO_2 \leftrightarrows N_2O_4$). When a temperature of approximately 50 °C or higher can be maintained, the reaction can be pushed to completion. Even under the less than ideal reaction conditions of Reaction #10, the mol% of CF_3NO_2 is still 83%. It is not difficult to envision that an increase in the reaction by a couple of degrees would have been enough to complete this reaction. For the low temperature Reactions #14–#17, the majority of the nitrogen dioxide reactant is in the N_2O_4 form, and far worse yields are observed. At these reduced temperatures so little $^\bullet NO_2$ is present that regardless of the stoichiometric ratio, no significant amount CF_3NO_2 is generated.

2.1.4. Effect of reaction time on the generation of CF_3NO_2

A set of experiments with stoichiometric ratios ranging from 1.5 to 2.1:1 of $^\bullet NO_2$:CF_3I, an initial ambient pressure of 0.15 atm, and a reaction temperature range of 41–49 °C was carried out for 1, 4, and 16 h. After 1 h of reaction time, the mol% of CF_3NO_2 generated was ~18%, while after 4 h, the mol% was ~59%, and after 16 h, the reaction had reached completion with a mol% of nearly 100%. Under ideal conditions, a reaction time of at least 16 h was required to achieve full conversion to CF_3NO_2 with the current experimental set-up. A few additional hours of reaction time were found to be helpful for reactions not being carried out under ideal conditions. Although reactions that were run up to 48 h suffered no adverse effects on conversion to CF_3NO_2, minimal changes in the mol% of CF_3NO_2 generated (+1 to +3%) were observed after 18–20 h of reaction time.

2.1.5. Percent yield

One goal of this research was to determine if isolated yields greater than 33–35% could be obtained [cf. 18]. Unfortunately, under these photochemical conditions, a yield greater than 33–35% could not be obtained. The radical reaction appears to be statistically driven with ~67% of the reaction forming the O-bonded intermediate (CF_3ONO), which irreversibly decays into COF_2 and FNO, while ~33% forms the desired N-bonded CF_3NO_2 molecule, which is stable under the 420 nm wavelength of light being used.
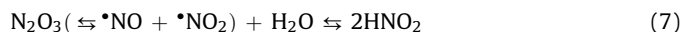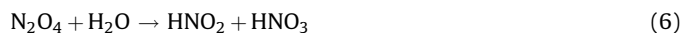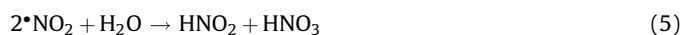
2.2. Bulk purification of CF_3NO_2

The initial purification method developed by the Thrasher group for CF_3NO_2 was both time consuming and complex. The

method was initially developed for the purification of SF_5NO_2, which requires much milder purifications conditions due to the relative weakness of the S–N bond [22,23]. This purification process involved a multi-step process of a trap-to-trap distillation followed by dry scrubbing of the resulting mixture over CsF, followed by another dry scrubbing over AlF_3, and finishing with another trap-to-trap distillation.

Although the aforementioned method is excellent for small-scale batches of 1–2 g of crude CF_3NO_2, upon increasing the amount to be purified to 5–10 g, several problems became evident. As the CsF and AlF_3 are used to purify the crude product mixture, they become deactivated. It was determined that ca. 2 g of CsF was required to purify 1 g of the initial crude product mixture. In the next purification step, it was found that ca. 1 g of AlF_3 was required for every 1 g of the product mixture. Also, 1–2 days of reaction time were required to complete each dry scrubbing step. The quick deactivation of the scrubbing materials coupled with the long time required to prepare anhydrous, amorphous AlF_3 (two weeks from the reaction of $AlCl_3$ and elemental F_2) led to the desire to find a more time- and cost-efficient method for purifying CF_3NO_2.

The unwanted chemical species remaining after the photo-chemical reaction are unreacted $^\bullet NO_2$ and sometimes CF_3I as well as the byproducts COF_2 and FNO, the latter of which reacts with glass, as well as any $^\bullet NO$ and N_2O_3 that might have been formed (see Eqs. (2) and (3)). All of these compounds, with the exception of CF_3I and the desired product CF_3NO_2, will be hydrolyzed in a caustic solution. The $^\bullet NO_2$ molecule is a major industrial pollutant, and caustic wet scrubbing methods have widely been used to remove $^\bullet NO_2$ from waste streams. The chemical reactions for the removal of $^\bullet NO_2$ by water and hydroxide are summarized below in Eqs. (5)–(10) [24,25].

$$2^\bullet NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \tag{5}$$

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3 \tag{6}$$

$$N_2O_3(\leftrightarrows {}^\bullet NO + {}^\bullet NO_2) + H_2O \leftrightarrows 2HNO_2 \tag{7}$$

$$3HNO_2 \rightarrow 2^\bullet NO + HNO_3 + H_2O \tag{8}$$

$$HNO_2 + OH^- \rightarrow NO_2^- + H_2O \tag{9}$$

$$HNO_3 + OH^- \rightarrow NO_3^- + H_2O \tag{10}$$

Eqs. (5)–(7) summarize the reactions of $^\bullet NO_2$ and its equilibrium partners in the presence of water. The generation of $^\bullet NO$ is not desired during this purification process because it has a low solubility in water and can escape from the aqueous solution and potentially combine with unscrubbed $^\bullet NO_2$ to form more N_2O_3, which will collect with the CF_3NO_2. The addition of caustic to the aqueous solution hinders the decay of HNO_2 into $^\bullet NO$, and as long as the feed to the scrubber is not too fast, one can prevent the formation of additional amounts of N_2O_3. Any N_2O_3 in the initial feed to the scrubber (cf. Eq. (3)) will be readily converted to nitrous acid as shown in Eq. (7).

The purification process for large-scale batches (10–100 g) of crude CF_3NO_2 requires several steps. For example, the crude product (ca. 10 g) from a number (5–10) of photolytic runs was collected in a stainless steel cylinder. The cylinder was then cooled to −78 °C to hold back the I_2 and most of the unreacted $^\bullet NO_2$. All of the CF_3NO_2, COF_2, FNO, and any unreacted CF_3I, if present, were then removed under dynamic vacuum into a −196 °C trap, as well as $^\bullet NO$ and some $^\bullet NO_2$ (and thus N_2O_3 and N_2O_4). The contents of the −196 °C trap were then transferred to another stainless steel cylinder for storage until future scrubbing with aqueous caustic.

For caustic scrubbing, the storage cylinder of crude CF_3NO_2 was attached to nitrogen-blanketed system containing two in-line

gas-washing bottles (500-mL capacity each with ca. 375 mL of 20 wt% aqueous KOH) followed by a product collection trap held at −196 °C leading to a nitrogen bubbler. The system was first purged with nitrogen gas before carefully switching the flow over to that from the storage cylinder. The bubbling rate, as seen in the first gas-washing bottle, should not exceed 1 bubble per second, and frits should be avoided due to a build-up of salts near the tip of the bubbler. The scrubbed gases are collected in the −196 °C trap, which is held at atmospheric pressure and followed by a nitrogen purge. At this point, the purified product will contain primarily CF_3NO_2, any unreacted CF_3I, and residual water. If either too fast of a bubbling rate is used or the caustic solution becomes expended, some N_2O_3 may be collected, as indicated by a deep royal blue color when condensed. Should this occur and in order to dry the purified product, the contents of the −196 °C trap were transferred into a cylinder containing dry KOH pellets. A quantity of pellets with ca. twice the mass of the purified CF_3NO_2 was used, and the contents of the cylinder were allowed to stand at room temperature overnight. The following day the cylinder was cooled to −78 °C, and the volatile contents were transferred into a clean, dry cylinder where only CF_3NO_2 (and any unreacted CF_3I) remained. If necessary, CF_3NO_2 can be separated from small amounts CF_3I by tedious trap-to-trap distillation with the traps set at −135, −155, and −196 °C (at ca. 15 mTorr). The CF_3I was stopped in the −135 °C trap, while CF_3NO_2 collected in the −155 °C trap. Due to these separation difficulties, unreacted CF_3I should be avoided if at all possible.

This new purification method drastically reduces the time required to obtain samples of pure CF_3NO_2. Several 100 g batches of crude product mixtures have been successfully purified using this method, and little preparation time or unique chemicals are required. The caustic solution can range from 1 wt% to a saturated aqueous solution; however, we generally used 20 wt% solutions. The CF_3NO_2 molecule is unaffected by exposure to caustic solution. As long as unreacted CF_3I is avoided, this method is significantly faster, less expensive, and more practical than the previous method of purification [18].

3. Experimental

3.1. Instruments

^{19}F, ^{14}N, and ^{13}C NMR spectra were recorded on either a Bruker AM 360 or AM 500 NMR spectrometer. NMR samples were prepared by first filling a 4-mm o.d. NMR tube topped with a Teflon® valve (Wilmad® J Young valve) with 600 Torr of pressure of the product mixture (post removal of most of the •NO_2). The contents of the NMR tube were then cooled to −196 °C, so that the solvent ($CDCl_3$) with reference standard (1 wt% CCl_3F) could be back condensed into the tube. Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer on gas samples (5–25 Torr) in a 10-cm glass cell fitted with silicon windows.

The photoreactor used was equipped with twelve 122-cm long diazo 40-W lamps (Philips TL40W/03) supported in the fashion of a palisade to give a 30-cm diameter inner chamber [18]. Each lamp was backed by a reflective panel in order to potentially give more passes of the diazo blue light back and forth through the reactor, which was place in the middle of the open chamber. The photoreactor system was also equipped with an exhaust fan for heat removal, when desired.

3.2. Starting materials

The starting materials CF_3I and •NO_2 are commercially available. The trifluoroiodomethane was used as received, while the nitrogen dioxide was checked prior to use for the presence of N_2O_3. This was accomplished by condensing the •NO_2 into a glass

trap held at −196 °C. If any blue color, N_2O_3, was observed, the trap was warmed to −78 °C and held under dynamic vacuum until all of the blue color disappeared (via removal of •NO and a shift of the equilibrium away from N_2O_3 [26]). The cesium fluoride was taken from laboratory stock, fused, and reground in a jar mill before use. The amorphous form of AlF_3 [27] was prepared via the fluorination of sublimed $AlCl_3$ with 20% F_2/N_2.

3.3. Synthesis of CF_3NO_2

An evacuated and tared ∼16.3-L Pyrex® glass reaction vessel was attached to the vacuum line and cooled to −196 °C. A total of 6.63 g (144 mmol) of •NO_2 was vacuum transferred into the vessel. After the reaction vessel was warmed back to room temperature, it was again weighed. The vessel was reattached to the vacuum line, re-cooled to −196 °C, and a quantity of 8.77 g (44.8 mmol) of CF_3I was added by vacuum transfer; again, the amount added was verified by differences in weight. The stoichiometric ratio of •NO_2:CF_3I was calculated to be 3.2:1, while the pressure in the reaction vessel at room temperature was calculated to be 0.30 atm. In all reactions, both the stoichiometric ratio and the pressure were calculated on the basis of •NO_2 being 100% of the equilibrium composition with its partner N_2O_4, which of course does not reflect reality but greatly simplifies the comparison of one reaction to another, especially since •NO_2 is being consumed during each reaction and thus the equilibrium is constantly shifting via Le Chatlier's principle. This oversimplification also makes sense when thinking about whether or not •NO_2 is truly the limiting reagent, especially in reactions that result in high mol% of CF_3NO_2 relative to CF_3I. The reaction vessel was then placed into the blue light reactor and irradiated for 18 h. This reaction yielded 1.40 g (12.2 mmol) of CF_3NO_2 following purification, representing a 27% yield. Trifluoronitromethane, CF_3NO_2, is a colorless gas with a boiling point of −32 °C [7].

3.4. Purification of CF_3NO_2

The contents of the reaction vessel are cooled to −196 °C and warmed slowly allowing the contents to be trapped in a −78 and −196 °C trap. The −78 °C trap collects unreacted •NO_2 and I_2 byproduct, while the −196 °C trap collects COF_2, CF_3NO_2, FNO, and unreacted CF_3I. The contents of the −196 °C trap are transferred into a fresh cylinder. The contents of the cylinder are pumped through two wash bottles containing 5–30% by weight caustic solution. The system is kept at 1 atm with N_2 and the material bubbled through the scrubber system is collected in a −196 °C trap. In order to both dry the CF_3NO_2 and remove any N_2O_3 (blue color), if present, the contents of the −196 °C trap are transferred into a clean, dry cylinder containing KOH pellets with at least twice the mass of the collected product. The contents of the cylinder are allowed to stand at room temperature overnight. The following day, the cylinder is cooled to −78 °C, and the contents are transferred into a clean, dry cylinder giving pure CF_3NO_2. If unreacted CF_3I is present in the final mixture, a trap-to-trap distillation must be carried out with traps held at −135, −155, and −196 °C. At a vacuum level of 15 mTorr, CF_3NO_2 is trapped in the −155 °C trap.

Spectral data of CF_3NO_2: the infrared, ^{19}F NMR, and ^{14}N NMR spectra of CF_3NO_2 matched data previously reported by others [2,11] and us [18]. A ^{13}C NMR spectrum was recorded [δ ($CDCl_3$): 113 (q) ppm, $^1J_{FC}$ = 298 Hz], and the data were consistent with those reported earlier by DeMarco et al. [16].

Acknowledgments

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