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# Solvent effects in the fluorination of 1,2-dichloro-1,1-difluoroethane (R-132b) to 2-chloro-1,1,1-trifluoroethane (R-133a)

Short communication

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#### Abstract

Trichloroethylene has been found to act as a rate enhancing co-factor in the liquid phase, tantalum (V) halide catalyzed, fluorine-for-chlorine exchange reaction of 1,2-dichloro-1,1-difluoroethane (R-132b) to 2-chloro-1,1,1-trifluorethane (R-133a). Several trifluoromethyl substituted benzenes have also been found to be rate-enhancing solvents.

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#### 1. Introduction

For decades chlorofluorocarbons have been useful chemicals for refrigeration, solvent, foam manufacture and firefighting applications. The refrigerant R-12 (CF<sub>2</sub>Cl<sub>2</sub>) was the standard refrigerant and found widespread use in automotive air conditioners. The discovery of the harmful nature of chlorofluorocarbons towards the Earth's protective ozone layer led to the outlawing of the manufacture and use of most of these chemicals in the 1989 Montreal Protecol. The most popular non-ozone depleting replacement for R-12 for use in automotive air conditioning units has been R-134a (CF<sub>3</sub>– CH<sub>2</sub>F). There are several manufacturers of R-134a in the US [1] as well as many overseas.

The production of R-134a generally begins with trichloroethylene (TCE) as feedstock. The processes are typically performed as two distinct reactions. First, TCE is fluorinated under catalytic conditions to 2-chloro-1,1,1-trifluoroethane (R-133a). This can be done in the liquid or vapor phase. In the second reaction, R-133a is further fluorinated to R-134a [2]. As this reaction is more difficult, it is most successfully performed as a high temperature vapor phase reaction over an alumina or chromia catalyst [3–6].

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Mechanistically, the first reaction can be broken down into three individual steps (see Scheme 1, Reaction 1). First, a molecule of HF adds across the TCE double bond to produce 1,1,2-dichloro-1-fluoroethane (R-131a). Second, direct fluorine-for-chlorine exchange converts R-131a to 1,2-dichloro-1, 1-difluoroethane (R-132b) [7–9]. The third reaction is another fluorine-for-chlorine exchange that converts R-132b to R-133a. In the normally vapor phase second reaction, R-133a is converted to R-134a (as the fourth and last individual step) (see Scheme 1, Reaction 2).

In the liquid phase reaction of TCE to R-133a, many transition metal halide Lewis acid catalysts have been reported to be effective. Antimony (V) halides are the benchmark catalyst for chlorine-for-fluorine exchange (Swartz reaction) but suffer from reduction to Sb (III) at temperatures above 80 °C [10]. The most current patent literature indicates that tantalum (V) halides and niobium (V) halides are the best choices for TCE to R-133a conversion [11–14]. In repetitions of the literature experiments, we found that tantalum (V) halides were superior to niobium (V) halides in converting TCE to R-133a.

Procedurally, these reactions were run at 140 °C. A blank run was performed without TCE, cycling catalyst and HF through the reaction warm-up and heating sequence in order to fluorinate TaCl<sub>5</sub> to TaF<sub>5</sub>. This would ensure that the catalyst was fluorinated for the first run to the same degree that it would be for subsequent runs. For each run, the conversion rate decreased with time as TCE concentration decreased and HCl

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pressure increased. While the reaction could be driven to completion with the venting of HCl pressure, reactions were considered complete when the TCE concentration was <5%. Without venting HCl, this TCE level remained unchanged with additional reaction time. Reactions were "complete" after 1.5 h at reaction temperature.

For every liquid phase fluorination reaction, a certain amount of oligomerization occurs, evidenced by the formation of higher boiling liquid by-products. Such by-products are referred to as "tars". It was observed that for 1-mol batch reactions of TCE to R-133a catalyzed by 4 mol% tantalum (V) halide, tar levels were around 9% (w/w). While the catalyst remained active through five consecutive batches, it is clear that in a continuous process the build-up of tars would eventually deactivate the catalyst.

In an effort to minimize the contact of tars with the expensive tantalum (V) catalyst, the reaction of TCE to R-133a was separated into its individual reactions. The working hypothesis was that tar generation occurred principally from oligomerization of the olefinic TCE. Conversion of R-131a to R-132b and R-132b to R-133a do not occur through an olefinic intermediate and so are expected to give lower tars. As such, one could potentially perform the HF addition to TCE with an inexpensive and expendable Lewis acid catalyst (i.e. TiCl<sub>4</sub>) and perform the more demanding, but cleaner fluorine-for-chlorine exchanges with the tantalum catalyst.

#### 2. Results and discussion

#### 2.1. Non-reactivity of R-132b

It was decided to test the hypothesis on the fluorination of R-132b to R-133a (rather than R-131a). The R-132b was isolated from the products of earlier TCE runs. After a blank, catalyst fluorinating run, the R-132b was added and heated to 140 °C precisely like the reference TCE reaction. Surprisingly, the reaction was extremely sluggish. After 1.5 h the conversion to R-133a was only 36%. A subsequent run had only 11% conversion and a third run, 3% conversion, even at high temperature (150 °C). What little activity the catalyst had, decreased quickly. The first instinct was to question the quality of "homemade" R-132b. A commercial sample was purchased and the experiment repeated, again first running a fluorinating run on the TaCl<sub>5</sub>. Results were again poor, in fact worse. A conversion of 22% for the first run was followed conversions of 1% for runs at 160 °C for as long as 12 h!

Next the catalyst came under suspicion. Perhaps the prefluorination runs were not converting  $TaCl_5$  to  $TaF_5$ , though the literature indicated that this was a facile process [11,15]. To

investigate this possibility, experiments were repeated on commercial R-132b with commercial TaF<sub>5</sub>. The procedure of Feiring [16], who reports the reaction of R-132b with HF and 2% TaF<sub>5</sub> at 100 °C, was followed closely. However, after heating to 100 °C followed by 20 h at 140 °C only 25% conversion to R-133a had occurred. Three hours at 160 °C did not change this result. This contradiction to the reported literature led us to consider the possibility that our catalyst was *too* fluorinated. Certainly, in the antimony (V) literature, it is well known that mixed chlorofluorides like SbCl<sub>2</sub>F<sub>3</sub> are active and highly soluble species [17]. Perhaps the reaction of TCE to R-132b is facile enough to generate an initiating concentration of HCl, which through equilibria, would prevent some or all of the catalyst from fluorinating completely to (apparently inactive) TaF<sub>5</sub>.

Two sets of experiments were undertaken to test this theory. First, an analysis was performed on the fluoride content of the tantalum (V) halide that was produced by treating TaCl<sub>5</sub> with HF at 140 °C. Invariably, the fluoride content of samples throughout this study were found to be 80% of theroretical for TaF<sub>5</sub>! This result indicates the empirical formula of "fully fluorinated" tantalum (V) to beTaClF<sub>4</sub> [18,19]. Also indicated is that this mixed halide is just as inactive as TaF<sub>5</sub> without TCE as a co-reagent.

The second set of experiments were to run R-132b + HF reactions with either  $TaF_5$  or  $TaClF_4$  under the pressure of at least 1 equiv. of anhydrous HCl gas. If  $TaCl_2F_3$ , etc. is the active species and *that* species is generated by fortuitous HCl from the preceding reaction steps, then this addition of HCl to the system should make for a reactive system. It did not. We observed no enhancement in the rate of R-133a formation.

#### 2.2. Reactivity of R-131b

The poor reactivity of R-132b under the tantalum halide catalyzed conditions made us question the mechanistic precept that  $R-131a \rightarrow R-132b \rightarrow R-133a$  proceeds by direct fluorinefor-chlorine exchange. While no olefinic intermediates were observed on GC chromatograms during the reactions of TCE, it was wondered whether saturated species were not necessarily the mechanistic intermediates on the pathway to fluorination. Possibly R-131a and R-132b are only observed because they are mechanistic dead-ends that have to revert back to an olefin (if not back to TCE) in order to fluorinate further. As such, R-131a would be expected to be relatively unreactive, similar to R-132b. Experimentally, the results were quite the opposite. At 110 °C, R-131a began reacting and within 1.5 h was completely consumed. The product was 22% R-133a and 74% R-132b. Interestingly, additional reaction time at 140 °C did not complete the conversion to R-133a. Again, R-132b was resisting fluorination under tantalum catalysis! In retrospect, this was not really surprising. In the reactions of TCE, R-132b concentrations build and then convert to R-133a while the R-131a concentration remains low and constant. Obviously the rate of conversion for R-131a to R-132b is faster than that of R-132b to R-133a. If the good reactivity of R-131a is attributed to its ability to eliminate to a mechanistically active olefin

(CFCl=CHCl) then the question still remains as to why R-132b does not do the same. The elimination of HCl from R-131a becomes thermodynamically favorable above 58 °C, while the elimination of HCl from R-132b becomes favorable above 82 °C [7]. In either case, reaction conditions have been above those temperatures.

#### 2.3. Catalytic activity of TCE and R-131b

One thing that had been evident in the original TCE experiments was that the reaction ceased to progress when the TCE levels fell to  $\sim 5\%$ . Originally, the simple assumption was made that the pressure of by-product HCl was restraining the equilibrium. However, even with venting of HCl, it was difficult to react out the last of the R-132a. It was now surmised that reactant TCE was possibly playing a role in accelerating the reaction of R-132b to R-133a. As such, this idea was tested by running R-132b to R-133a reactions spiked with TCE.

A prefluorinating reaction of HF with 4% TaCl<sub>5</sub> (versus anticipated R-132b) was run, followed by attempted reaction of R-132b without TCE in order to establish that the system was non-reactive. To this non-reactive system was added 10 mol% TCE and the reaction resumed. Within 15 min the conversion to R-133a was 87% (with 60% of the TCE remaining). At 1.75 h conversion was >99% (with only 40% of the TCE remaining). The reaction was stopped, vented and *only* R-132b was recharged. Upon reheating, the reaction again initiated. Conversion at 1.75 h was 99%. Upon reaching reaction temperature, TCE was down to 0.4% and was nearly undetectable throughout the reaction. Batch reactions could be run to completion indefinitely by charging 15% TCE into every other run.

As has been noted above, the reaction of pure R-131a to R-133a proceeds, but mostly produces R-132b. We noted at this point that the R-131a level had decreased to 2%. It seemed possible that the reaction had "hung-up" because, like TCE, R-131 was a component that could make for an active system. In practice, this appears to be true as a non-reactive R-132b reaction, as prepared above, became reactive with the addition of 15 mol% R-131a. The reaction appears to be a bit slower than the TCE activated reaction until one realizes that 90% of the R-131a had reacted as well as the R-132b. As such, at 1.75 h the conversion was 99%.

#### 2.4. Mode of activity of TCE and R-131a

With the strong evidence for the critical role of TCE and/or R-131a in the fluorine-for-chlorine substitution reaction of R-132b to R-133a, several possible modes of activity were considered. They were, chloride source, catalyst complexing agent and solvent effect.

*Chloride source.* The concept of TCE or R-133a acting as chloride ion sources was explored above when the mixed halide nature of the tantalum chlorofluoride catalyst was investigated. That role was thus discounted.

*Complexing agent*. A simple solvent effect is an unlikely cause for reaction enhancing properties of TCE or R-131a. The

solubility of HF in TCE is much lower than that of HF in R-132b. As one might expect, the more fluorinated species solubilizes HF to the greater extent. Further, the catalyst is almost exclusively dissolved in the HF, and the resulting ionic solution even less miscible with the organic phase. The possibility that TCE was forming a soluble complex with the tantalum halide catalyst was explored by running reactions with the close TCE analogs, 1,2-dichloroethylene and tetrachloroethylene. In short, neither chloroolefin enhanced the reaction. Reactions of R-132b with up to an equal volume of t-1,2-dichloroethene exhibited only 8% conversion after 23 h. Similarly, after 50 h in the presence of tetrachloroethylene, only 33% conversion of R-132b to R-133a had occurred. Both versions of the reaction could be "rescued" and taken to high conversion with the addition of TCE. It appeared, then, that if TCE were acting as a complexing agent at all, the structural requirements for activity were very specific. (It should be noted that tetrachloroethylene and dichloroethylene are themselves rather unreactive to tantalum/HF conditions [16] and maintained a good concentration throughout the course of the reaction trials.)

Solvent effect. At this point, the simple solvent effect as cause for the reaction enhancing properties of TCE or R-131a was begging to be investigated. As such, several alternative solvents were screened to see if simple solvation could enhance the reaction rate. Solvents were chosen on their ability to withstand HF/Lewis acid conditions and their potential for use on industrial scale (some were even chosen for their potential complexing ability). Each solvent was scoped for activity by testing it with R-132b and preformed TaClF<sub>4</sub>. Exploratory reactions were performed where the solvent was used in equal volume to the R-132b substrate as well as at the 15% level where TCE had good enhancing effect.

The straight-forward solvent perfluorononane showed no enhancement activity. Nor did the straight chain, but polar perfluorooctanesulfonyl fluoride, nor the aromatic and polar benzenesulfonyl fluoride. R-133a was tested as an obvious choice, but also showed no activity. Success came quickly with the use of *m*-(bis)-trifluoromethylbenzene (see Fig. 1). Truthfully, this solvent was chosen by hypothesizing on a bidentate Lewis base, one with  $-CF_3$  pincers. While the reactivity was welcome, the pincer theory was quickly discounted when *p*-(bis)-trifluoromethylbenzene was found to be equally active as a rate enhancing agent. However, now it was surmised that strong solvation of the catalyst was coming as a result of catalyst complexation by the aromatic ring [20]. Follow-up



Fig. 1.  $R-132b \rightarrow R-133a$  conversion with equal volume of solvent.



Fig. 2.  $R-132b \rightarrow R-133a$  conversion with 15% volume of solvent.



Fig. 3. R-132b  $\rightarrow$  R-133a conversion with equal volume of a nitro-benzotrifluoride.

testing was performed to see how much or how little electronwithdrawing effect was allowable to make for an activating aromatic system.

A single  $-CF_3$  or a single -Cl substituent is insufficient to empart reaction enhancing ability. Benzotrifluoride (trifluoromethylbenzene) and chlorobenzene offered no enhancement. However the paired combination of  $-CF_3$  and -Cl did. Both *m*-chlorobenzotrifluoride and *p*-chlorobenzotrifluoride were rate-enhancing solvents. Negative results for *m*difluorobenzene indicates that two fluorine substituents are not enough to impart activity. However, pairing a  $-CF_3$  group with a single F, as *m*-fluorobenzotrifluoride, afforded another rate enhancing solvent.

Interestingly, at equal volume, all three "mixed" aromatics lagged behind the (bis)-trifluoromethylbenzenes. However, at the 15% level, the reactivities were on par (see Fig. 2).

The pairing of a nitro substituent with a trifluoromethyl group also makes for an activating aromatic solvent, but only in one of the three cases. *m*-Nitrobenzotrifluoride enhanced the rate of R-132b to R-133a conversion, but to a lesser extent than any other active solvent. *o*- and *p*-Nitrobenzotrifluoride showed no enhancement activity. Interestingly, *m*-nitrobenzotrifluoride exhibited an induction period of about 1 h where it showed zero activity (see Fig. 3). Once the enhancement began, the reaction proceeded with a linear increase in conversion from then on. This curious result is under active investigation.

Pairing two nitro groups was not sufficient to make an activating solvent. No reaction was observed with *m*-dinitrobenzene in the reaction mixture.

#### 3. Conclusion

The conversion of 1,2-dichloro-1,1-difluoroethane to 2-chloro-1,1,1-trifluoroethane (R-132b  $\rightarrow$  R-133a) does not

readily occur in liquid hydrogen fluoride with tantalum (V) halide catalysis. A co-reagent of trichloroethylene or 1,1,2-trichloro-1-fluoroethane (R-131a) is required in 10–15% molar concentration to affect full conversion. Alternatively, a solvent of  $CF_3$ -, F-, Cl- or NO<sub>2</sub>-substituted benzotrifluoride can also effect the conversion.

The nature and action of these and other co-reagents is under investigation and will be reported when sufficient data is collected to define the mechanism of action.

#### 4. Experimental

#### 4.1. General

Anhydrous hydrogen fluoride was Matheson-Trigas CP grade. Trichloroethylene was PPG Fluorocarbon Grade TR/119 and was used without removal of inhibitor. Trifluoromethyland fluoro-substituted benzenes, perfluorononane, perfluorocarbon Synquest Labs. R-133a was from Halocarbon. Tantalum (V) chloride was NOAH Technologies 99.99%. Tantalum (V) fluoride, *t*-dichloroethylene, tetrachloroethylene, chlorobenzene and dinitrobenzenes were Aldrich. Benzene sulfonyl fluoride was prepared *in situ* from J.T. Baker benzene sulfonyl chloride. Reactions were performed in a Parr 300 mL hastelloy minireactor. GC was performed on an HP 5730A spectrometer with a 60 M DB-1 capillary column.

*Cautionary note.* Anhydrous HF causes *instantaneous* severe burns to the skin and mucous membranes. HF should be handled with full PPE protection. An ample supply of HF antidote gel should be kept on hand before handling HF. See reference for burn treatment procedures [21].

## 4.1.1. Example 1. Hydrofluorination of R-132b in the presence of 15% trichloroethylene enhancer

Seven hundred and twenty milligrams (0.004 mol) of TaCl<sub>5</sub> was charged to the reactor. The reactor was evacuated and cooled with ice. Fifty grams (2.5 mol) of anhydrous hydrogen fluoride was charged. The solution was heated with stirring to 140 °C for 1 h. The reactor was again cooled with ice. A mixture of 13.4 g (0.1 mol) 1,2-dichloro-1,1-difluor-oethane and 1.97 g (0.15 mol) trichloroethylene was injected and the reactor heated to 140 °C. Samples were drawn from the reactor headspace and the reaction was monitored by GC. See Fig. 2 for results.

## 4.1.2. Example 2. Hydrofluorination of R-132b in the presence of 15% 1-fluoro-1,2,3-trichloroethane (R-131a) enhancer

Seven hundred and twenty milligrams (0.004 mol) of TaCl<sub>5</sub> was charged to the reactor. The reactor was evacuated and cooled with ice. Fifty grams (2.5 mol) of anhydrous hydrogen fluoride was charged. The solution was heated with stirring to 140 °C for 1 h. The reactor was again cooled with ice. A mixture of 13.4 g (0.1 mol) 1,2-dichloro-1,1-difluoroethane and 2.2 g (0.15 mol) 1-fluoro-1,2,3-trichloroethane was injected and the reactor heated to 130 °C. Samples were drawn

from the reactor headspace and the reaction was monitored by GC. Conversion at 1 h was 87.5%.

## 4.1.3. Example 3. Hydrofluorination of R-132b in the presence of equal volume solvent enhancer

Seven hundred and twenty milligrams (0.004 mol) of TaCl<sub>5</sub> was charged to the reactor. The reactor was evacuated and cooled with ice. Fifty grams (2.5 mol) of anhydrous hydrogen fluoride was charged. The solution was heated with stirring to 140 °C for 1 h. The reactor was again cooled with ice. A mixture of 13.4 g (0.1 mol) 1,2-dichloro-1,1-difluoroethane and 10 mL of the chosen solvent was injected and the reactor heated to 140 °C. Samples were drawn from the reactor headspace and the reaction was monitored by GC. See Fig. 1 for results.

### 4.1.4. Example 4. Hydrofluorination of R-132b in the presence of 15% volume solvent enhancer

Seven hundred and twenty milligrams (0.004 mol) of TaCl<sub>5</sub> was charged to the reactor. The reactor was evacuated and cooled with ice. Fifty grams (2.5 mol) of anhydrous hydrogen fluoride was charged. The solution was heated with stirring to 140 °C for 1 h. The reactor was again cooled with ice. A mixture of 13.4 g (0.1 mol) 1,2-dichloro-1,1-difluoroethane and 1.5 mL the chosen solvent was injected and the reactor heated to 140 °C. Samples were drawn from the reactor headspace and the reaction was monitored by GC. See Fig. 2 for results.

#### 4.1.5. Example 5. Preparation and analysis of TaClF<sub>5</sub>

101.0 g (0.28 mol) TaCl<sub>5</sub> was charged to the reactor. The reactor was cooled with dry ice/acetone. One hundred and twenty five grams (6.25 mol) of anhydrous hydrogen fluoride was charged. The solution was heated 3 h. The reaction was cooled in a water bath to 30 °C and the HCl pressure vented. The reactor was held then under aspirator vacuum for 60 min. The vacuum was broken with N<sub>2</sub> and the reactor opened in a glove box. 74.25 g (91%) of yellow-brown solid was isolated.

One hundred and forty five milligrams of solid was dissolved in 500 mL 15% sodium acetate buffer solution and analyzed versus standard 100 ppm  $F^-$  with a fluoride selective electrode. The analysis was 81 ppm. A check sample of 145 mg TaF<sub>5</sub> had an analysis of 100 ppm.

## 4.1.6. Example 6. Attempted hydrofluorination of R-132b with additional hydrogen chloride

Five hundred and forty milligrams (0.002 mol) of  $TaF_5$  was charged to the reactor. The reactor was evacuated and cooled

with ice. Fifty grams (2.5 mol) of anhydrous hydrogen fluoride was charged. 13.4 g (0.1 mol) 1,2-dichloro-1,1-difluoroethane was injected. Then 3.6 g (0.1 mol) anhydrous hydrogen chloride was injected and the reactor heated to 140  $^{\circ}$ C for 3 h. No reaction occurred. The reactor was cooled with ice and an additional 5.8 g (0.16 mol) of anhydrous hydrogen chloride was injected, pressurizing the reactor to 200 psi. The reaction was heated to 140  $^{\circ}$ C for 3.5 h. No reaction was observed.

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