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THE USE OF IR SPECTROSCOPY TO MONITOR THE CONVERSION OF MATRIX ISOLATED PHENYLACETYL CHLORIDE TO PHENYLACETYL CATION, WITHOUT DECARBONYLATION TO BENZYL CATION

RONALD M. JARRET*, NY SIN AND TIMOTHY RAMSEY
Department of Chemistry, College of the Holy Cross, Worcester, Massachusetts 01610, USA
MARTIN SAUNDERS
Department of Chemistry, Yale University, New Haven, Connecticut 06511, USA

ABSTRACT

IR spectroscopy is presented as a convenient means to monitor the formation of acyl (and alkyl) cations from corresponding acid chlorides, with Lewis acids at low temperature in the solid state. Phenylacetyl chloride is co-deposited (under vacuum at −173 °C with antimony pentafluoride on a KBr window, as in the 'molecular beam' method of cation generation. The initial IR spectrum of the deposition shows (in addition to starting materials) that a small amount of phenylacetyl cation (2274 cm^{-1}) has been formed. Warming the solid matrix to −123 °C promotes the smooth conversion of acid chloride to acyl cation. Ultraviolet irradiation (through quartz windows) at −123 °C to −73 °C facilitates this conversion but does not result in the loss of carbon monoxide from the acyl cation to form benzyl cation. When benzyl chloride is used in place of phenylacetyl chloride, there is no noticeable difference between IR spectra taken before and after warming and/or photolysis of the solid deposition.

INTRODUCTION

A number of substituted benzyl cations have been studied as stable species with NMR[1], but observation of the parent (C_7H_7) cation has not been reported in the literature. The conventional approach[2] to sample preparation through ionization of benzyl chloride with antimony pentafluoride in solution, leads to uncontrolled polymerization. Ionization of the halide apparently occurs so slowly that it cannot escape attack by ions present in solution. There has been limited success with attempts to overcome this problem through extreme dilution, using the molecular beam method.[2] The main evidence[3] indicating that benzyl cation was generated is the decrease and disappearence of peaks (3·3 and 9·4 ppm) at −20 °C, with the simultaneous appearance of a single peak (with an observed ^{13}C side-band) which is consistent with tropylium cation. If the spectrum represents the benzyl cation (and not a complex between the alkyl halide and acid), there is indication that the parent ion's structure

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*Author for correspondence.

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may be quite dissimilar to substituted (stabilized) benzyl cations.[1,4] While a small percentage of samples have generated ^{1}H-NMR spectra with the described peaks, the extreme dilution and lack of reproducibility between samples make systematic investigation impossible.

Chemical precursors other than benzyl halides are possible. Benzocyclopropene (C_7H_6) is a potential precursor to benzyl (or norcaradiene) cation. The aromatic compound is prepared[5] in ample quantity and adequate purity from readily available starting materials; however, protonation proceeds with less reliability. None of the twenty-five samples prepared (differing in precursor concentration, precursor – acid ratio, and 'magic acid' composition), show any indication of the presence of benzyl cation.

6-Methylenebicyclo[3.1.0]hex-3-en-2-yl cation is another possible precursor to benzyl cation. Ionization of 6-methylenebicyclo[3.1.0]hex-3-en-2-yl chloride[6] readily generates the corresponding C_7H_7 cation. Below $-110\,°C$, the NMR spectrum represents a static cation with C_2 symmetry. As the temperature is increased to $-70\,°C$, peaks (5·6, 7·5, 9·6 ppm) broaden into the baseline; the effect is reversed by a reduction in sample temperature. The observations are consistent with the degenerate circumambulation of one ring about the other (E_a = 10·6 kcal/mol). At temperatures above $-70\,°C$, the sample decomposes to unidentifiable products, without detection of the symmetry forbidden rearrangement to benzyl cation.

Decarbonylation of acyl cations[7] is another general approach for generating carbocations. Acyl cations usually form readily in solution when acid halides are ionized with Lewis acids. Thermally activated conversion of acyl cations to the corresponding carbocation (with loss of carbon monoxide) is possible when the resulting carbocation is particularly stable (tertiary, etc.). Since initial acyl cation formation occurs readily and completely, conversion of the acyl cation to the corresponding carbocation need not be swift to avoid polymerization (assuming that the acyl cation and carbocation will not interact). The preparation of benzyl cation by this approach requires that decarbonylation of phenylacetyl cation proceed without rearrangement to the stable tropylium ion.

Mixing phenylacetyl chloride with antimony pentafluoride in sulfuryl chloride fluoride generates a stable solution of phenylacetyl cation.[8] Concentrated phenylacetyl cation solutions remain stable up to 25 °C but decompose to unidentifiable products at higher temperatures. Thus, thermal decarbonylation of phenylacetyl cation in solution is not a viable route to the benzyl cation. When an NMR tube (pyrex) containing a solution of phenylacetyl cation is photolyzed with a high intensity mercury lamp at $-140\,°C$ to $-70\,°C$ for up to 12 hours, no changes are observed in the ^{1}H-NMR spectrum. Photolysis at higher temperatures enhances decomposition to unidentifiable products.

It would be of considerable interest to develop a method which facilitates the preparation of benzyl (and other elusive) cation(s) at sufficiently high concentration so as to permit further experimentation. It is with this intention that IR spectroscopy is used as a means to monitor cation formation in the solid state, at low temperature.[9]

DISCUSSION AND RESULTS

In an attempt to develop a reproducible means of benzyl cation generation, treatment of cation precursors in the solid state (rather than in solution) is employed. Following the steps of the conventional molecular beam approach[2] to cation preparation, a solid matrix containing the precursor in antimony pentafluoride is deposited in the reaction vessel. Before solvent is added, the solid deposition is treated (warming to temperatures above liquid nitrogen and/or photolysis for prolonged periods of time) to promote cation formation under conditions of restricted.mobility. The solvent is then added, and the sample preparation continues as usual. The NMR spectra of benzyl chloride and phenylacetyl chloride samples, prepared in this manner, do not differ from corresponding samples which are prepared without treatment of the solid deposition. To discover if warming and/or photolysis of the solid matrix promotes cation production, a means of spectroscopic observation of the solid during (or immediately after) treatment is essential.

While the absence of solvent may eliminate undesirable interactions during cation generation, it also precludes the convenient use of solution NMR as a means to observe cation formation. Low temperature solid state ^{13}C-NMR is a possible means for monitoring the ionization process, but spectroscopy of this nature is cumbersome. Synthesis of isotopically enriched precursors, low temperature magic angle spinning (to resolve carbonyl signals of the acyl cation and acid chloride which are about 25 ppm apart in solution) and ^{19}F decoupling[10] (to remove coupling to antimony pentafluoride) are required.

Since both acid chlorides and acyl cations have strong and distinct absorbances in the infra-red region,[7] IR spectroscopy is ideally suited for monitoring cation formation in this system. It is also appropriate for the detection of decarbonylation, and it does not suffer from the drawbacks of solid state NMR spectroscopy. A cryogenic displex unit is used to co-deposit phenylacetyl chloride and antimony pentafluoride on a KBr window, under vacuum at low temperature. The conditions are designed to mimic that of the molecular beam method of cation generation.[2] The turnable displex shroud is equipped with opposing KBr plates for IR spectral acquisition and a quartz plate which allows unobstructed irradiation of the sample. If these conditions indicate carbocation generation, the effective treatment of the sample would be repeated in a reaction vessel that mimics the displex-experimental conditions but allows for convenient addition of sulfuryl chloride fluoride, to permit solution NMR spectroscopy.

The IR spectrum (Figure 1a) taken immediately after the deposition at −173 °C, shows (in addition to phenylacetyl chloride and antimony pentafluoride) that phenylacetyl cation has been generated. The tiny and relatively sharp band at 2274 cm^{-1} is evidence for cation (or partial cation) formation, in the solid state. This band is not present in the background scans, or the neat phenylacetyl chloride or antimony pentafluoride. The band position matches that reported (2279 cm^{-1}) for the CO stretch of $PhCH_2CO$—SbF_6 (mull) at room temperature.[7] The most intense band centered at 1797 cm^{-1} corresponds to the carbonyl stretch in phenylacetyl chloride.

Periodic acquisition of IR spectra at increased sample temperature (up to −123 °C) allows for observation of the controlled conversion of phenylacetyl chloride to phenylacetyl cation (Figure 1b). The band at 2274 cm^{-1} becomes more intense as the band at 1797 cm^{-1} diminishes in intensity; a new band at 1685 cm^{-1} also emerges. Unfiltered photolysis (high intensity Hg lamp) and/or elevated temperatures (−73 °C) facilitates the conversion of acid chloride to acyl cation (Figure 1c). Increasing the sample temperature in combination with direct photolysis, however, does not promote decarbonylation in this system.

When benzyl chloride is used in place of phenylacetyl chloride, IR spectra before and after treatment of the solid deposition are not noticeably different. That is, the IR spectrum of benzyl chloride in an antimony pentafluoride matrix after hours at −173 °C to −73 °C (with or without photolysis) is comparable to the combination of spectra of benzyl chloride and of antimony pentafluoride. Since no estimate of the time required to ionize benzyl chloride can be made from the IR experiment, a sample of benzyl-α-^{13}C chloride in antimony pentafluoride was prepared for solid state NMR spectroscopy. While very noisy, the static fluorine-coupled solid state CMR spectrum[11] shows only slight changes after weeks at −78 °C. These small

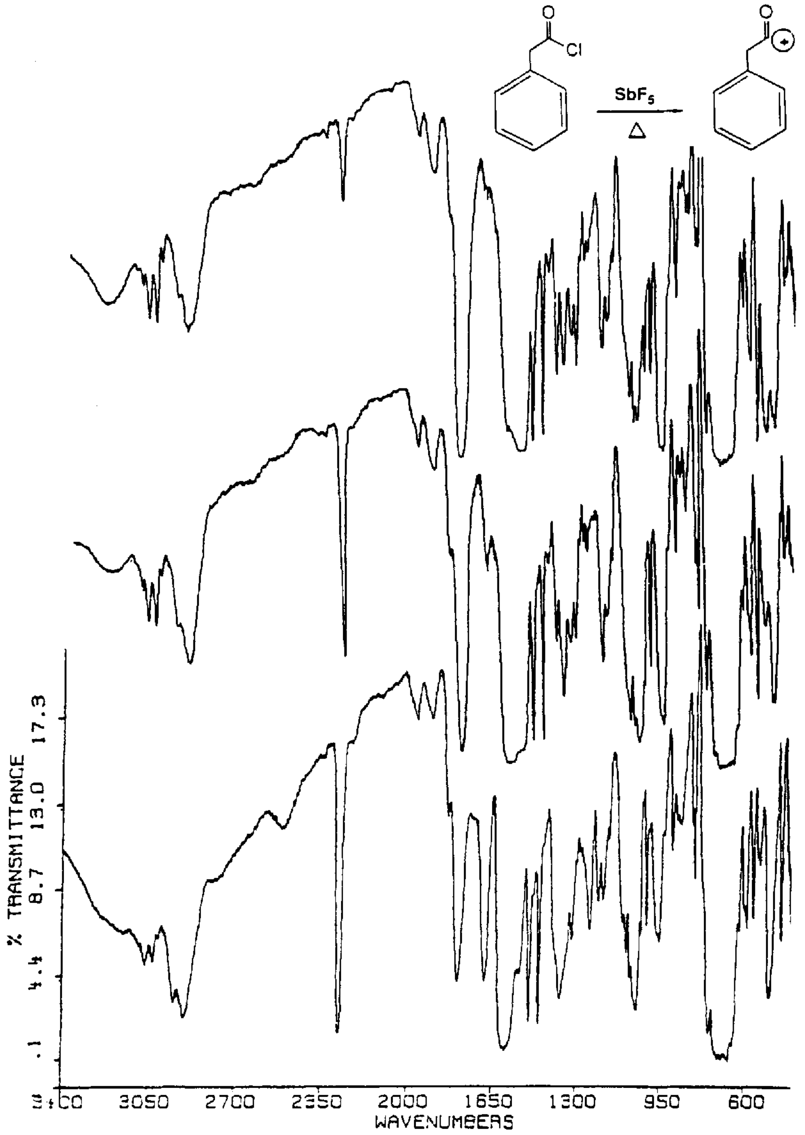

Figure 1. Phenylacetyl chloride in an SbF_5 matrix. (a) Upper: IR spectrum after deposition at −173 °C. (b) Middle: IR spectrum after three hours at −123 °C. (c) Bottom: IR spectrum after three hours at −73 °C

changes (which may represent ionization of benzyl chloride), occurring over such a long period of time, indicate that the use of the 'displex-IR' as a means to monitor cation formation in the solid state is simply impractical for benzyl chloride/cation.

CONCLUSIONS

Low temperature solid state IR spectroscopy is an ideal means for monitoring the production of acyl cations from the corresponding acid chlorides in an antimony pentafluoride matrix.

With spectral acquisitions of the substrate in the ionizing environment, before extensive cation formation takes place, unambiguous assignments are made. Sample preparation is easy and sample decomposition is not a concern. While this approach has not proven useful in the preparation of benzyl cation from phenylacetyl chloride (or benzyl chloride), this technique would allow for the direct spectroscopic observation of acyl cations which are unstable at room temperature because of facile decarbonylation. Cation formation and decarbonylation in such systems, would be readily controlled and observable with this application of variable temperature IR spectroscopy.

EXPERIMENTAL

The spectra are recorded on a Nicolet 7199 high resolution FT-IR spectrometer. A cryogenic displex unit is used for sample deposition and temperature control. The square, turnable, head is equipped with opposing KBr windows and opposing quartz windows. The shroud is designed to mimic the 'molecular beam' method of cation generation. One face has two 1/16″ inlet (o-ring lined) holes, focussed on a 1 mm thick KBr plate (supported in the center of the chamber). The arm of the displex unit can be lowered into the IR spectrometer cavity for spectral acquisitions (through the KBr windows) and raised for photolysis (through the quartz windows, after rotation of the shroud).

The substrate and antimony pentafluoride are introduced from sample holders, through copper tubing (1/4″ glass to 1/4″ copper tubing, with a swagelock connector; 1/4″ copper tubing to 1/16″ copper tubing, welded together). Phenylacetyl chloride and benzyl chloride are purchased from Aldrich Co., and antimony pentafluoride is obtained from Columbia Cationics Co.; each reactant is distilled just prior to the deposition.

The system is evacuated to approximately 10^{-6} torr and the KBr plate is cooled to $-173\,^{\circ}\mathrm{C}$. The antimony pentafluoride valve is opened first, followed by the phenylacetyl chloride valve. After one minute, the valve to the acid chloride is closed and then the flow of antimony pentafluoride is also halted. The sample temperature can now be altered and/or the sample photolyzed; an Oriel 6283 mercury vapor lamp (200 watt) was used.

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