Haloaldehyde Polymers. 47.[†] Analysis of Linear *tert*-Butoxide-Initiated, Acetate-Capped Chloral Oligomers by Potassium Ionization of Desorbed Species[‡]

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ABSTRACT: Linear *tert*-butoxide-initiated, acetate-capped chloral oligomers were analyzed by mass spectrometry using potassium ionization of desorbed species (K+IDS). This technique allowed us to study oligomers of mass numbers up to 1500 Da. Oligomers with mass numbers from the [unimer]K^+ (302 Da) to the mass of 1187 Da, the [heptamer]K^+, could be identified. Individual oligomers were also characterized by chlorine isotope analysis. The mixtures of the lower oligomers were also analyzed by GC.

Introduction

For the past decade we have been working on the development of rules that govern the synthesis of helical polymers and have used the polymerization of trichloroacetaldehyde (chloral) (and other perhaloaldehydes) as the most promising examples.[1-5]

This work has proceeded in several directions, two of which are relevant for this discussion: (a) initiation of chloral polymerization and oligomerization with achiral initiators (*tert*-butoxide);[6-8] (b) spectral characterization of individual oligomeric species and determination of their absolute configuration.[9-12]

We found that when chloral was initiated with an achiral initiator such as *tert*-butoxide, the first addition product consisted of a racemic mixture of the unimers. As further additions of chloral to the first addition product proceeded, the addition progressed with increasing stereospecificity to oligomeric alkoxides. Meso addition became predominant over racemic addition. The tetramer already has the structure of an exclusive all-meso configuration; further additions of chloral units are exclusively in meso configurations, which led to the isotactic-specific polymerization of chloral. This increased stereospecificity had been predicted by minimum-energy calculations of the linear chloral dimers and trimers. Although the first addition of chloral to the racemate of the chloral-terminated alkoxide is essentially random (equal amount of meso/racemic addition), isotactic polychloral is finally formed exclusively.

The oligomers obtained from chloral addition to *tert*-butoxide were acetate capped and—now in a stable form of a "frozen" equilibrium of the oligomerization—were characterized. The m dimer, the mm trimer, the mmm tetramer, and the mmmm pentamer were isolated and crystallized. Their absolute configuration was determined by single-crystal X-ray crystallography.[9,11] The results of these analyses confirmed our earlier prediction that stereospecific and conformational specific addition that lead to polychloral must lead to an isotactic helix (4/1, or actually an 11/3, helix) for polychloral.

Mass spectrometry is a very good method for identifying organic compounds of reasonably low molecular weight by studying their ions in the gas phase. This method has become a powerful technique for identifying organic compounds rapidly, specifically, and with high sensitivity. Earlier mass spectrometric work examining compounds containing trichloromethyl groups by direct mass spectrometry has shown that such compounds undergo extensive fragmentation with the initial loss of the trichloromethide group (followed by further fragmentation), making the direct mass spectrometric analysis of trichloromethylated compounds impossible.

Other mass spectrometric techniques involving chemical ionization have become available and have proved to be superior in many cases to direct mass spectrometry for the analysis of sensitive compounds. One of the newest mass spectrometric techniques is a potassium ionization technique, called K+IDS (K^+ ionization of desorbed species). Ionization of chemical compounds in the presence of potassium ions gives pseudo molecular ions in the form of [M]K^+. This very mild method does not degrade most (even sensitive) organic compounds. The instrumentation and the technique allow the detection of ions with molar masses up to 2000 Da. What is detected are the ions of the molar mass numbers plus that of the potassium ion of 39 Da.[13-15]

We have selected K+IDS for the determination and characterization of oligomers of perhaloacetaldehydes. The ionization technique is based on the thermionic emission of potassium ions from a matrix containing potassium ions. It provided an excellent method for examining our perhaloaldehyde oligomers up to mass numbers of about 1500 Da; a preliminary report of our investigation has been presented.[16]

Experimental Section

A. Materials. Chloral (Montrose Chemical Co.) was heated under reflux for 1 day over phosphorus pentoxide (granules, 50 g/L of chloral); it was then distilled into a flask that had been flamed out and allowed to cool under a flow of dry nitrogen. The flask was connected to a fractional distillation apparatus that was equipped with a 1.2-m-long column packed with glass helices. With careful exclusion of air (<2 ppm oxygen) chloral was heated under total reflux for several days and then distillation was started. In the early stages, the distillation was kept at reflux

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[‡] This paper is dedicated to Professor Henri Benoit on the occasion of his 70th birthday with our warmest wishes.

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ratios between 100:1 and 50:1.[26] During this entire time, dry oxygen-free nitrogen was used to protect the system against atmospheric oxygen and moisture. Gas chromatography was used to monitor the purity of the distillate. When the purity reached levels of at least 99.9%, the distillation was terminated and a constant reflux was begun. Monomer grade (purity in excess of 99.9%) was distilled as needed and was used immediately.

n-Butyllithium (1.6 M, in hexanes), lithium metal (99%), *tert*-butyl alcohol, methylcyclohexane (anhydrous), and acetic anhydride (ACS reagent) were obtained from Aldrich Chemical Co. and were used without further purification. Lithium *tert*-butoxide (Alfa Products) was sublimed at 150 °C and 0.1 mmHg before use. For the large run, lithium *tert*-butoxide was prepared from *tert*-butyl alcohol and *n*-butyllithium in methylcyclohexane, and the solution was used immediately for the initiation of the chloral oligomerization.

B. Measurements. A Varian 3000 gas chromatograph with a 50 cm × 5 mm stainless steel column packed with 100/200 Chrom G.H.P. coated with 5% OV101 or a 1.5 m × 5 mm column packed with 80/100 Chrom Q11 coated with OV17 was used to analyze the oligomers and to characterize the purity of the "polymerization-grade" chloral. The column temperature was programmed for a constant 2.5 °C/min rate of temperature increase from 130 to 250 °C.

The mass spectrometric experiments were performed on a Finnigan 4615B quadrupole GC/MS system. An EI source configuration was used in all K+IDS experiments. The ion source pressure (ion gauge) was $<10^{-6}$ Torr with a source temperature of 200 °C. For a more detailed explanation of the experimental procedures involved in the K+IDS technique, consult ref 15.

C. Procedure. *tert*-Butoxide-Initiated, Acetate-End-Capped Linear Chloral Oligomers (TBIAC): Large Run. Lithium *tert*-butoxide was prepared by dissolving lithium metal (6.9 g, 1 mol) under reflux in an excess of *tert*-butyl alcohol (200 mL); the excess *tert*-butyl alcohol was removed under a reduced pressure of 0.1 mmHg.

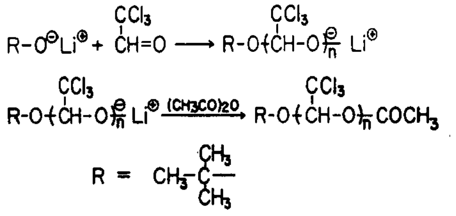
A 5-L three-neck, round-bottom flask equipped with a mechanical stirrer, a dropping funnel, and a gas inlet and outlet was flamed out and allowed to cool to room temperature under dry nitrogen. Lithium *tert*-butoxide and methylcyclohexane (800 mL) were added to the flask. After the lithium *tert*-butoxide was dissolved, the solution was warmed to 50 °C. Polymerization-grade chloral (737 g, 5 mol) was added slowly via the dropping funnel while the temperature of the reaction mixture was kept around 50 °C. The solution was then allowed to cool slowly to 35 °C, and acetic anhydride (510 g, 5 mol) was added to the vigorously stirred solution to end-cap the oligomeric alkoxides. After the addition was complete, the mixture was stirred for an additional 2 h; it was then allowed to stand overnight at room temperature. Water (1 L) was added to the mixture with continued vigorous stirring. The organic layer was allowed to separate, and the aqueous layer was extracted with dichloromethane; the combined organic solutions were filtered [some polychloral powder was collected (5 g, yield 0.6%)]. The filtrate was then washed twice, first with 5% aqueous sodium bicarbonate and then with water. It was then dried over anhydrous magnesium sulfate. After removal of the solvent with a rotary evaporator, a viscous liquid consisting primarily of linear chloral oligomers remained; yield 840 g (98%). Fractional distillation under reduced pressure gave a unimer fraction boiling at 67–70 °C/0.1 mmHg; yield 593 g (74%). The dimer fraction was collected at 117–120 °C/0.1 mmHg; yield 186 g (24%). Eight grams (1%) of a trimer fraction was collected at 150–170 °C/0.07 mmHg. The residue (3 g, 0.4%) consisted of the tetramer and fractions of higher oligomers.

The dimer fraction was allowed to stand at room temperature for over 1 year, during which time one of the diastereomeric dimers crystallized slowly. After recrystallization twice from methanol, a pure dimer stereoisomer was obtained, mp 62–64 °C.

Anal. Calcd: C, 29.20; H, 3.41. Found: C, 29.19; H, 3.32.

The polychloral (17 g) obtained in this reaction was extracted in a Soxhlet extractor for 2 days with dichloromethane. After removal of the solvent, 0.4 g of a mixture of higher chloral oligomers, a white solid, was obtained.

Scheme I



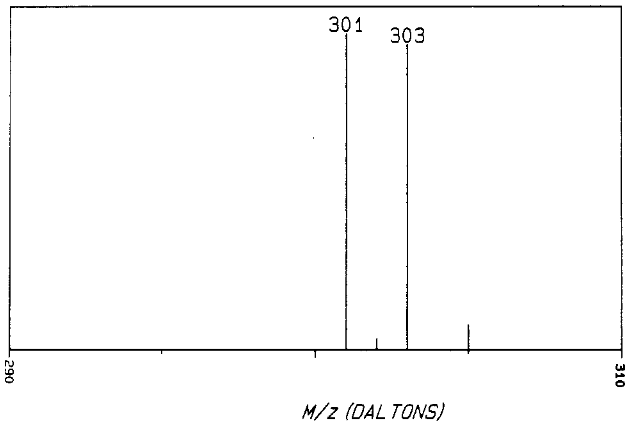


Figure 1. Mass spectrum of *tert*-butoxide-initiated, acetate-capped unimer (m/z 303).

Results and Discussion

Chloral oligomerization initiated with *tert*-butoxide followed by end-capping with acetic anhydride was carried out (Scheme I). A mixture of linear chloral oligomers was obtained that (according to GC analysis) consisted of a mixture of compounds including one unimer and two dimers (the result of meso and racemic addition), some trimers, the tetramer, and a very small amount of higher oligomers.

Mass spectrometry is an exceedingly useful tool for the identification of organic compounds or the identification of individual compounds in mixtures such as our linear chloral oligomers. Mass spectrometry can analyze individual components by identifying their mass ions, but it cannot distinguish individual stereoisomers of the same mass. We have found that K+IDS mass spectrometry could be used for the identification of the amounts of the individual compounds of molecular weight fractions of stereomeric oligomers of TBIAC. Samples of a TBIAC oligomer mixture were briefly studied by GC and NMR spectroscopy before.[7]

The K+IDS spectrum of the unimer $[M]K^+$ of the TBIAC is shown in Figure 1. Figure 2 shows the mass spectrum of the purified crystalline mm dimer $[M]K^+$, which shows a cluster of ions centered at 449 Da. The cluster is due to the isotopic distribution of chlorine atoms in the molecule. Although the compound is 99.9+ pure according to GC, a trace amount of a compound with a mass peak at 597 Da, the trimer $[M]K^+$, as well as a small peak at 435 Da is still noticeable. The peak at 435 Da corersponds to the mass of the potassium-attached dimer diacetate of chloral. Figure 3 shows the mass spectrum of a cluster of ions that is centered on the mass of the trimer ($[M]K^+ = 597$ Da); the dimer ($[M]K^+ = 449$ Da) can also be seen as well as the tetramer ($[M]K^+ = 743$ Da). A small amount of the pentamer ($[M]K^+ = 891$ Da) is also noticeable.

In Figure 4 the fraction of higher chloral oligomers centering on the tetramer is shown as analyzed by K+IDS mass spectrometry. The figure shows the predominant peak at a mass of 745 Da, the tetramer $[M]K^+$, as the main

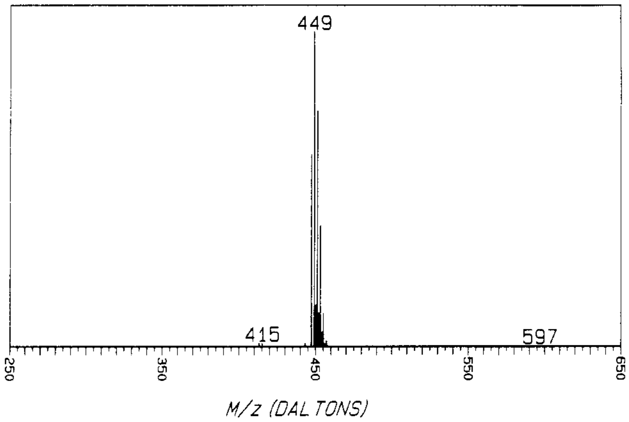


Figure 2. Mass spectrum of *tert*-butoxide-initiated, acetate-capped dimer (m/z 449).

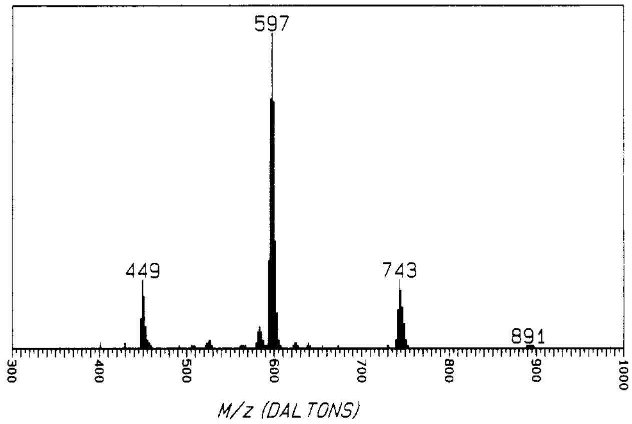


Figure 3. Mass spectrum of *tert*-butoxide-initiated, acetate-capped trimer fraction (m/z 597).

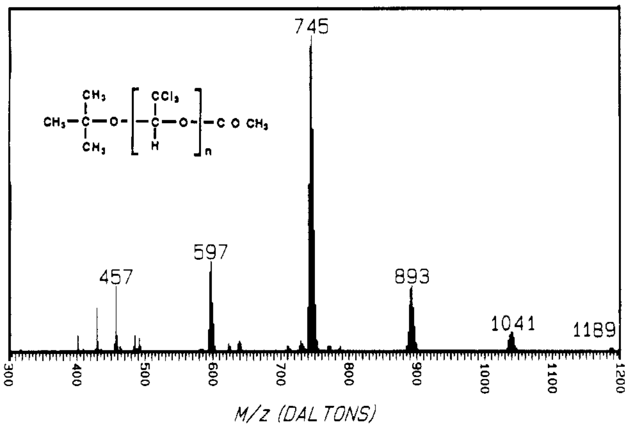


Figure 4. Mass spectrum of *tert*-butoxide-initiated, acetate-capped high oligomers (centered major mass peak at m/z 745).

component; substantial amounts of the trimer ([M]K$^+$ = 597 Da) can also be seen. We can also recognize in Figure 4 a compound with the mass number 893, the pentamer [M]K$^+$. other peaks with higher mass numbers can also be identified in the figure. Since the concentration of the higher oligomers in the oligomer mixture is very small, the attenuation of the intensity was increased by a factor of 10 for compounds of mass numbers in excess of 1000 Da. This allowed a more accurate identification of the hexamer ([M]K$^+$ = 1041 Da) as well the heptamer ([M]K$^+$ = 1187 D). Higher oligomers seem to be present but have not been detected as yet by our mass spectrometric technique.

As a byproduct of the chloral oligomerization we obtained in all oligomerizations (followed by acetate capping) also the acetylation product of the unchanged monomer chloral, chloral diacetate [M]K$^+$ = 288 (Figure 5).

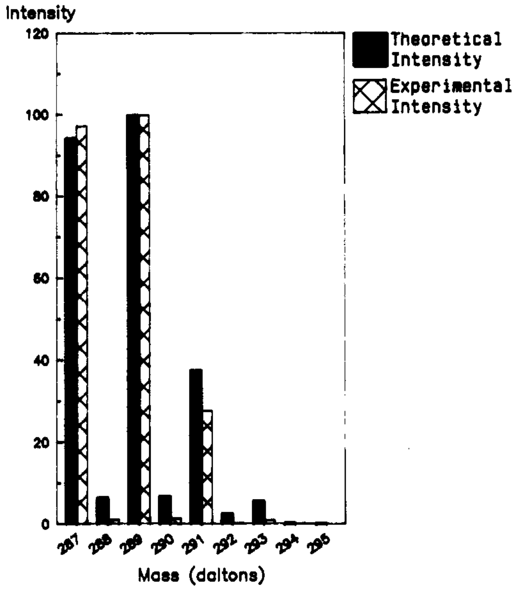


Figure 5. Isotope analysis of chloral diacetate (m/z 288).

The analysis of linear oligomers of chloral by K+IDS has provided a rich harvest of results by the qualitative and quantitative analysis of the linear oligomers produced by *tert*-butoxide initiation of chloral followed by acetate end-capping of the oligomeric alkoxide mixture. Further refinement of the method will undoubtedly allow us to identify trace amounts of even higher linear chloral oligomers. A mixture of small amounts of these oligomers was isolated by exhaustive Soxhlet extraction of the insoluble chloral polymer but their identification was not possible with our present K+IDS setup. The compounds have a relatively high molecular weight and consequently have low volatility. These higher oligomers were found to be less soluble, were very strongly attached to the chloral polymer, and required exhaustive Soxhlet extraction to be separated from the polymer.

The chloral unit in the TBIAC has three chlorine atoms in the trichloromethyl groups, which provides an additional dimension for a detailed analysis of the structures of these highly chlorinated compounds by analysis of the isotope distribution of the individual oligomers.

In the TBIAC series we have analyzed the unimer [M]K$^+$ to the heptamer [M]K$^+$. We present in Figure 6 the results of the isotope analysis of the TBIAC [dimer]K$^+$. We have also calculated the theoretical isotope distributions for the octamer [M]K$^+$, the nonamer [M]K$^+$, and the decamer [M]K$^+$; the latter is shown in Figure 7. The last three oligomers have not yet been observed in our mass spectra.

We will present and discuss as an example of the isotope analysis the TBIAC [dimer]K$^+$ (Figure 6). The same approach was used to compute the theoretical peak distribution for the isotope distribution of all chlorine-containing oligomers. We are describing here in more detail the calculation of the chlorine isotope distribution for the [dimer]K$^+$. The molecular formula of the TBIAC [dimethyl]K$^+$ is $C_{10}H_{14}O_4Cl_6K$. The predicted pattern resulting from the six chlorine atoms can be calculated

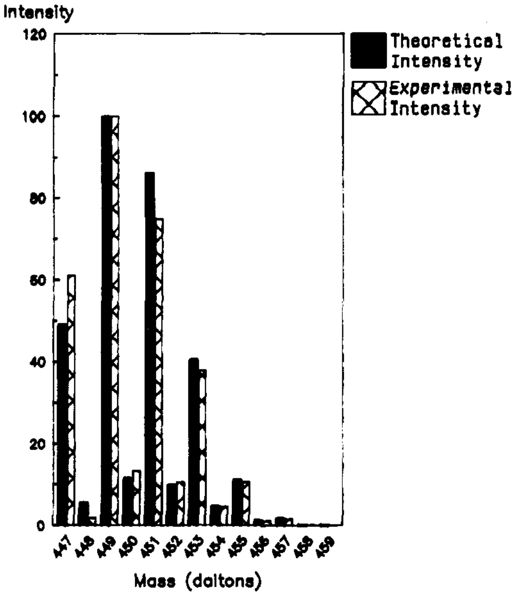


Figure 6. Isotope analysis of *tert*-butoxide-initiated, acetate-capped dimer (m/z 449).

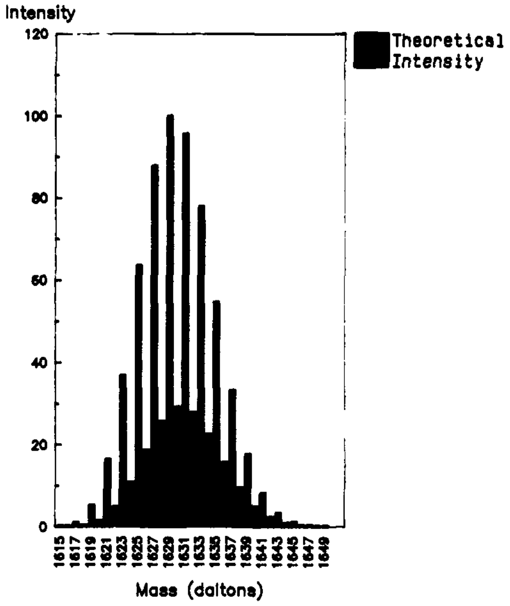


Figure 7. Theoretical isotope analysis of *tert*-butoxide-initiated, acetate-capped decamer (m/z 1631).

from the binomial expansion[18]

$$(a+b)^n = a^n + na^{n-1}b + n(n-1)a^{n-2}b/2! + n(n-1)(n-2)a^{n-3}b^3/3! + \ldots$$

where our specific case has $n = 6$, $a = 1$, and $b = 0.325$, the relative abundance of the chlorine-37 isotope.

For the six chlorine atoms we calculate a distribution of M (51.3%), M + 2 (100%), M + 4 (81.3%), M + 6 (35.2%), M + 8 (8.58%), and M + 10 (1.12%). In addition to the distribution arising from multiple chlorine atoms, potassium possesses two significant isotopes for ^{39}K (100%) and ^{41}K (7.4%). These isotopes must be considered in the isotope distribution calculations. ^{12}C (100%) and ^{13}C (1.1%) will also be accounted for in our analyses. The isotopic contributions of ^{2}H (0.015%), ^{17}O (0.04%), ^{40}K (0.01%), and ^{18}O ().2%) will not be included due to their low abundance. In all cases we will use the integer nuclidic masses in our computations. The theoretical isotope distribution of the TBIAC dimer [M]K$^+$ is presented in Table I.

Table I
Theoretical Isotope Distribution of the TBIAC Dimer MK$^+$

mass	calcd abundance	mass	calcd abundance
447	43.06313	454	4.668745
448	5.689496	455	11.26678
449	100	456	1.285668
450	11.5708	457	1.828956
451	86.22468	458	0.2063553
452	9.947068	459	0.161228
453	40.64434		

Figure 6 presents the comparison (in bar chart form) of the theoretical and the experimental results. We have found in most cases excellent agreement between the theoretical isotope distributions and our experimental results, thus corroborating the proposed structures of all our TBIAC oligomers.

For the analyses of the TBIAC oligomers we did not use exact masses but only integer masses. The use of the exact masses for chlorine (34.9689 Da, 75.47% abundance, instead of 35 for the chlorine-35 isotope, and 36.9659 Da, 24.53% abundance, instead of 37 for the chlorine-37 isotope) becomes increasingly important as the number of chlorine atoms exceeds 20. This correction only affects the specific positioning of the mass axis, but not the profiles of the ions. We also did not discuss other sources of uncertainty as they are of exceedingly small importance.

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