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SHORT-LIVED CARBONIUM IONS OF RETINYL ACETATE[1,2]

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Many articles are found in the literature which report that conjugated polyenes will form molecular species referred to as carbonium ions when placed in a proper acid media. Deno (1) has done considerable work on the carbonium ions generated from compounds containing two conjugated double bonds in either cyclic or linear systems. The existence of these carbonium ions was verified by examining changes in freezing point depression, kinetic data, as well as bathochromic wavelength shifts. De Vries (2) postulated the same carbonium ion intermediate for the protonation of 1,2,4,4-tetramethyl-3,5-dimethylenecyclopentene and for hydride abstraction from hexamethylcyclopentadiene. One of the more recent characterizations of carbonium ions is given in the comprehensive work by Sorensen (3) involving the preparation and reactions of a homologous series of aliphatic polyenylic cations. In 1959 Wassermann (4) pointed out that the addition of trichloroacetic acid to retinyl acetate (λmax 330 mu) gave a shift in the

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[1] Nomenclature for vitamin A acetate proposed by the Commission of Biological Chemistry of the International Union of Pure and Applied Chemistry (1960).

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λmax to 650 mu which he attributed to the formation of a "protonated vitamin A acetate."

Recent work in this laboratory has shown that reactions of retinyl acetate with several Lewis acids and trichloroacetic acid give essentially the same absorptions for the initial species generated. Therefore, on the basis of this experimental work, the authors would like to correct certain λmax values for carbonium ions which have appeared in the literature.

While attempting to reproduce Wassermann's work, it was found that by lowering the temperature of the solutions and by rapidly scanning the visible spectrum immediately after mixing there is an unstable product formed which gives rise to several other products. The procedure involves the mixing of 2 mg of retinyl acetate (6.09×10^{-6} mole) and 1.8 g of trichloroacetic acid (1.1×10^{-2} mole) in 25 ml of cooled benzene. Immediately after mixing, a sample of the solution is scanned from 900 to 500 mu using the repetitive scan attachment on the Beckman DK-2A Ratio Recording Spectrophotometer. To eliminate any spectral deviation due to temperature changes, a constant temperature cell was used to keep the solution just above the freezing point of benzene.

Repetitive scan revealed the growth of a single peak which reached its maximum at about two minutes. A decrease in absorption of this peak was accompanied by the growth of two peaks on either side of the initial peak. It is believed that the λmax reported by Wassermann which he attributed to the protonated retinyl acetate is in fact an absorption value for one of the polymers generated after the formation of the initial carbonium ion. This unstable carbonium ion has a λmax of 604 mu in benzene and is quite short-lived. Cationic polymerization of this initial carbonium ion then begins, and various polymer products are formed which absorb at different wavelengths. One of these polymers absorbs at longer wavelengths than the initial carbonium ion and is the wavelength reported by Wassermann.

It was found that by changing solvents a different λmax for the initial carbonium ion is obtained, and a different polymerization path is followed. The results of many experiments are summarized in Table I. The polymeric products formed are apparently similar when either behzene or toluene are used as solvents. In either case, two main polymers are formed which have absorptions in the visible region that are close to the initial carbonium ion. Polymerization in 1,2-dichloroethane is less complex since only one product is found which has an absorption in the range of from 900 to 500 mu.

TABLE I

Wavelengths of Carbonium Ions from the Retinyl Acetate-Trichloroacetic Acid Systems

Solvent	Average Molar Ratio (base*:acid)	Average Cell Temperature (°C)	Average λmax# of carbonium ion (mu)
benzene	1:1805	7-8	604
toluene	1:1806	7-8	602
1,2-dichloro-ethane	1:185	4-4.5	586

*2 mg retinyl acetate (6.09 x 10^{-6} mole)

#approximately 30 sec. after mixing

Lewis acids have long been known to react with conjugated polyenes to form products which absorb at much longer wavelengths. The Carr-Price reaction (5), for example, is used to detect the presence of vitamin A compounds by the formation of a deep blue color when 25% antimony trichloride in chloroform is added. Inhoffen, et al, (6) have also used this reaction to characterize the vinylogs of vitamin A. In this laboratory we have studied the generation of carbonium ions from Lewis acids of Group VA elements. It was observed that only a single peak was produced initially in each case; and as its intensity decreased, other peaks were found to develop. The resulting data from Group VA Lewis acids are summarized in Table II. Wavelengths for the initial carbonium ions agree favorably with that of the carbonium ion reported in Table I. In the latter case, a proton acid is used in the same solvent.

TABLE II

Wavelengths of Carbonium Ions from Retinyl Acetate and Group VA Lewis Acids

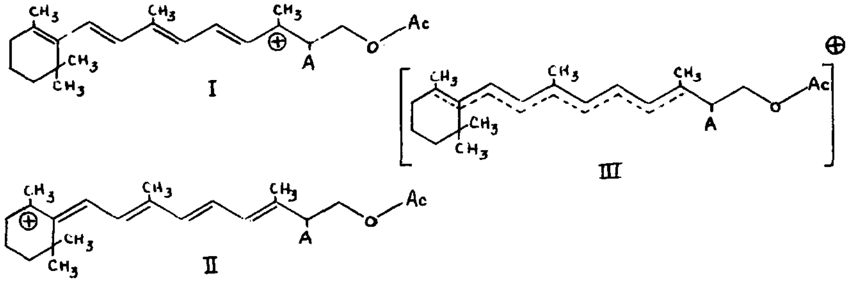
Lewis Acids	Molar Ratio (base*:acid)	Solvent	Cell Temp. (°C)	λmax‡ of carbonium ion (mu)	Other λmax (mu)
PCl_3	1:36	1,2-DCE	-31	561	897,606
$AsCl_3$	1:720	"	"	577	909,588
$SbCl_3$	1:90	"	"	589	878

*2 mg retinyl acetate (6.09 x 10^{-6} mole)

‡approximately 30 sec. after mixing

As already stated, the Lewis acids were reacted with retinyl acetate under conditions similar to those used for proton acids. Only the molar ratios of the substituents were varied. The values reported for each Lewis acid are those which gave the best spectra. In each case, the amount of retinyl acetate used and the total volume of solution (25 ml) remained the same. The other wavelengths reported are for absorptions which developed after the initial carbonium ion formation.

On the basis of the information above, it seems logical to conclude that the initial carbonium ions are identical, regardless of whether a proton or Lewis acid is used. Structures I and II represent the limiting resonance structures for the initial carbonium ion in which the acid (A) has been added to the carbon-carbon double bond. The positive charge is not localized on any one carbon atom but is distributed over all of the sp^2 carbon atoms. The unusually stable resonance hybrid thus obtained may be represented by structure III.



I

II

III

The polymer products generated after initial carbonium ion formation are also ionic species. Treatment of the acidic solution with aqueous base, water and anhydrous calcium chloride gives a solution containing neutral polymers. As expected, the absorption spectra undergoes a blue shift. The spectra of the neutral solutions were scanned from 900 to 280 mu. There was no absorption observed from 900 to 425 mu, indicating a complete neutralization of charged species. A diluted (10:1) portion of the quenched solution revealed several absorption peaks and shoulders in the region from 425 to 280 mu. These absorptions would be equivalent to the different polymers formed from the initial carbonium ion.

In a separate experiment, one hour after mixing, solutions of neutral polymers were prepared and the molecular weights determined using the Mechrolab Vapor Pressure Osmometer, Model 301A. Average molecular weights were determined in benzene and 1,2-dichloroethane. In the former solvent, the average molecular weight of the polymers was 1076 g per mole or roughly 3.3 times greater than the original retinyl acetate. In the latter solvent, the average molecular weight was 1470 g per mole or an increase of 4.5 times in molecular weight.

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