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Short communication

Lifetime of benzyl-*gem*-diacetate in aqueous solution

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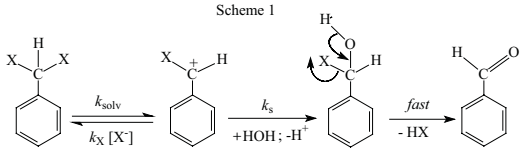
Conditions for the solvolysis of benzyl-*gem*-diacetate were established and the lifetime of benzyl-*gem*-diacetate was determined.

Key words: Lifetimes, benzyl-*gem*-diacetate, solvolysis.

Solvolysis of benzyl-*gem*-dihalides and benzyl-*gem*-diazides in water were carried out in our laboratory [1, 2] and the mechanism suggested, was as given below.

Scheme 1



X = N_3, Cl, Br, and CH_3COO

But the solvolysis did not take place at all when X = CH_3COO. Few possible explanations of reluctance of solvolysis or the extraordinary stability of benzyl-*gem*-diacetate in water has been explained in detail in our previous publication [3], based on the arguments of leaving group inability, the nucleophilicity, hydration energies of anions, and the geminal interactions of acetate groups on the ipso carbon. Since the solvolysis of benzyl-*gem*-diacetate did not proceed, (for the reasons stated above), we had resorted to acid catalysis [4].

EXPERIMENTAL

Kinetic studies employed in the present work are similar to our earlier studies [1, 2]. Buffers of pH 6.0, 5.5, 5.0, 4.5, 4.0 and 3.5 were prepared using acetic acid and sodium acetate. Kinetic studies in these buffers were performed and k_{solv} estimated. The concentration of benzyl-*gem*-diacetate in each of the buffer was 0.1 mM and an ionic strength of 0.1M was maintained with KCl in each of the buffer. The stock solution of the compound, benzyl-*gem*-diacetate, was stored in HPLC grade acetonitrile. All reactions were followed on Kontron uv-visible spectrophotometer and calculations were carried out using Kalaidagraph (USA) software. The chemicals used for this study were acetic acid and sodium acetate (both of analytical grade).

RESULTS AND DISCUSSION:

The kinetic studies at different pH values were carried out. A plot of k_{solv} vs [H^+] (See Table 1) was plotted and the k_{solv} at zero [H^+] i.e. in pure water was determined by interpolating the data to zero [H^+]. The results are shown in Figure 1.
Earlier study of benzyl-gem-diacetate [3] demonstrated the reluctance of the compound to undergo solvolysis. In this work, conditions for the solvolysis were established by using different acidic buffer solutions. Kinetic studies were carried out by following the product benzaldehyde.

Table 1. Rate constants for the solvolysis of benzyl-*gem*-diacetate at different pH in aqueous solution.

pH	[H^+]	k_{solv}/s
3.5	3.16 X 10^{-4}	1.03 X 10^{-2}
4.0	1.0 X 10^{-4}	4.8 X 10^{-3}
4.5	3.16 X 10^{-5}	2.28 X 10^{-3}
5.0	1.0 X 10^{-5}	1.14 X 10^{-3}
5.5	3.16 X 10^{-6}	4.92 X 10^{-4}
6.0	1.0 X 10^{-6}	4.62 X 10^{-4}

Thus the reciprocal of the k_{solv} would give lifetime of the compound in water, which turned out to be 1140 seconds. The mechanism in acid catalyzed path is made known in Scheme 2. As is evident in Scheme 2, the result of protonation leads to the conversion of acetate ion to acetic acid, which is a better leaving group; hence it departs with ease

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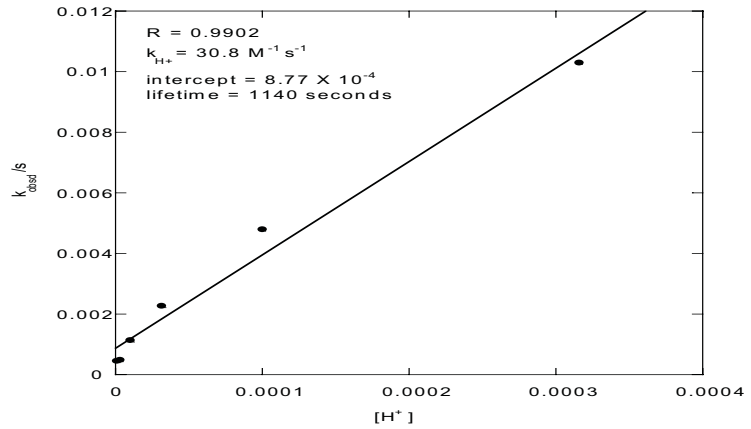
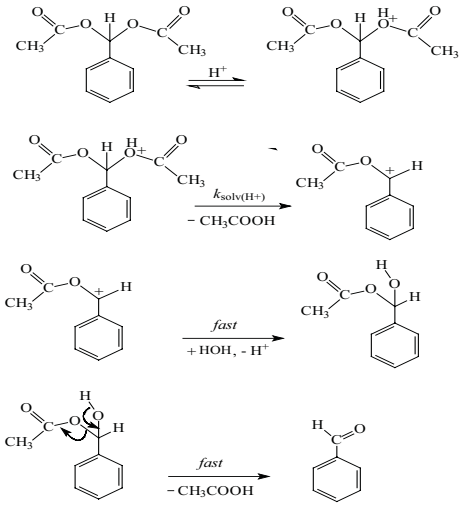


Fig. 1. Plot of k_{solv} vs. hydrogen ion concentration



Scheme 2

relative to acetate ion. Therefore it was possible to observe acid catalysis in the reaction.

The lifetime of benzyl-gem-diaceatate was estimated to be 1140 seconds from the interpolation of plot of k_{solv} *vs.* [H^+]. This study, i.e. the lifetime determination of benzyl-gem-diacetate, is reported for the first the time. This is the novelty of this piece of work.

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ПРОДЪЛЖИТЕЛНОСТ НА СЪЩЕСТВУВАНЕТО НА БЕНЗИЛ-*gem*-ДИАЦЕТАТ ВЪВ ВОДНИ РАЗТВОРИ

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(Резюме)

Установени са условията на солволиза на бензил-*gem*-диацетат, като е определена и продължителността на съществуването му.