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Determination of Lifetimes of Carbocations in Aqueous Solution by azide clock: A Simple Physical-Organic Chemistry Experiment

A simple and relatively new protocol is described in this article for the determination of the lifetimes of carbocations in aqueous solution.

Carbocations usually have lifetimes of the order of a few nanoseconds.

A very important intermediate in many organic reactions is the carbocation. As the name implies, carbocation is an organic cation containing a positively charged carbon. It has only a sextet of electrons surrounding the charged carbon and is therefore quite reactive. Originally they were called carbonium ions. The parent member is the methyl cation (CH_3^+). On the strength of kinetic studies, Meerwein and Van Emster [1] suggested the intermediacy of carbocations in solution as early as the 1920s. Since then numerous new organic compounds were discovered and synthesized. This requires knowledge of the stability and reactivity and the lifetime of these cations. The history of the field is well documented in the form of reviews with titles of 'carbonium ions' and 'reactive intermediates' [2].

The lifetime of a carbocation is nothing but the reciprocal of the rate coefficient (k_s) for its disappearance in a given solvent. If water is the solvent, then we will denote the rate constant by $k_{\text{H}_2\text{O}}$. As the lifetime of the reactive intermediates would normally be in the range of a few nanoseconds, its experimental determination usually needs relatively expensive fast reaction techniques like flow methods, pulse radiolysis or laser flash photolysis methods. Therefore, it is quite interesting that the lifetime of the carbocations generated under solvolytic conditions in an undergraduate or postgraduate physical-organic chemistry laboratory can be determined by a competition kinetic technique.

The laser flash photolytic generation of carbocations by Steenken *et al* [3] in the presence of various nucleophiles, which allowed the direct determination of the rate constants for reaction between the

Keywords

Lifetimes, carbocations, azide clock.



carbocation and the nucleophile to be roughly between $10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ and the diffusion limited value close to $5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$, was a major breakthrough in the investigation of these intermediates. Among the various nucleophiles studied, the azide ion (N_3^-) was found to be the most reactive. It reacts with any carbocation (with some exceptions like highly stabilized tri-p-anisyl methyl cation ($\text{p-MeOC}_6\text{H}_4)_3\text{C}^+$) with a rate constant of $5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$. These second order rate constants together with the (pseudo) first order rate constants ($k_{\text{H}_2\text{O}}$) can be used to determine the lifetime of the carbocation. (See equation (4) for relation between these two).

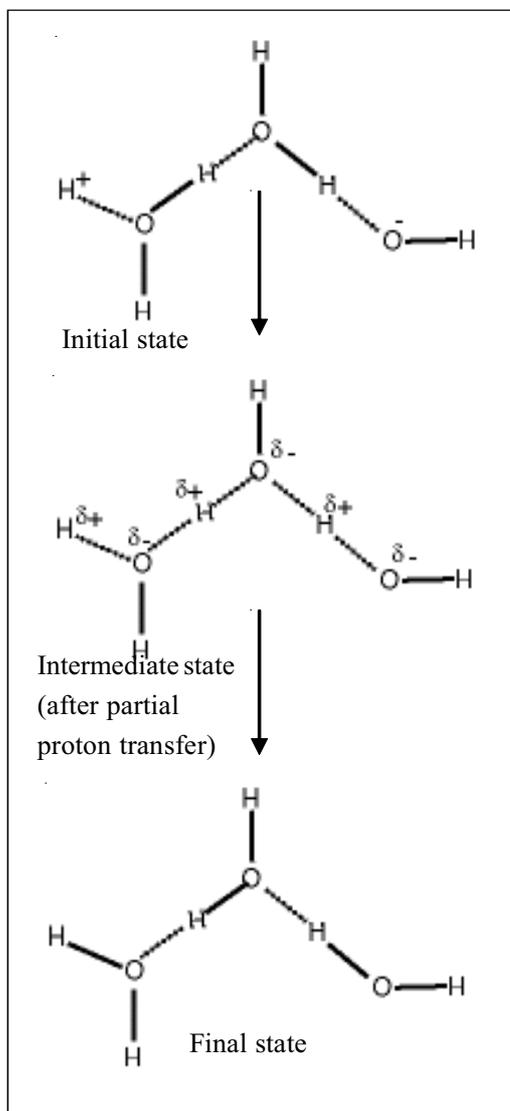
At this point it is necessary to know the meaning of diffusion and activation controlled reactions. If the reaction occurs whenever two molecules of reactants come together, then the reaction is limited by the rate of their coming together. There is no (or little) activation energy for the reaction and the rate is just the encounter frequency and the reaction is said to be diffusion controlled. An example is the combination of H^+ and OH^- for which the rate constant is $1.4 \times 10^{11} \text{ dm}^3 (\text{mol. sec})^{-1}$! Note that this rate constant is much larger [4] than the one determined directly by Steenken *et al* [3] for a typical diffusion controlled reaction. The encounter frequency imposes an upper limit on the rate of the reaction. As such the proton and hydroxide ion are much smaller in size and can move faster in aqueous solution than any other molecule, by the Grothus mechanism. The rate constant for a diffusion-controlled reaction is relatively independent of the nature of the chemical species and temperature. The typical activation energy for such reactions is in the range 8–14 kJ mol^{-1} (2–4 kcal mol^{-1}). The mechanism suggested for the reaction of H^+ and OH^- is that the ions come together by diffusion, after which neutralization occurs by proton jumps from one neighboring water molecule to another as shown in *Scheme 1*.

In comparison to diffusion limited rate constants, the activation limited rate constants are affected strongly by a change in temperature.

Laser flash photolytic technique is a fairly expensive method for the determination of the lifetime. In this article, a simple method for the

Diffusion controlled reactions have little or no activation energy.



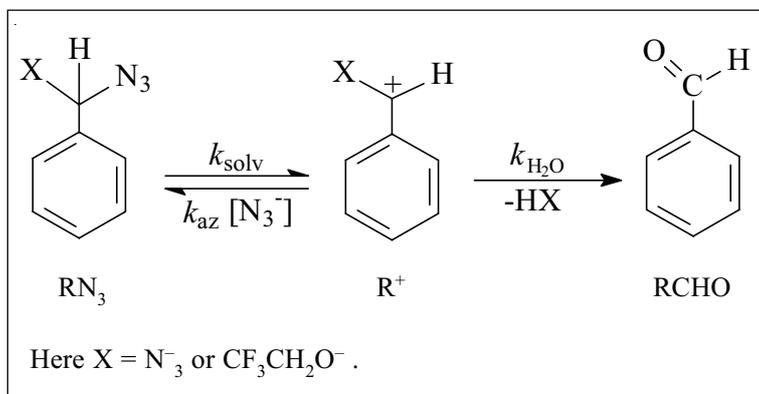


Scheme 1.

determination of the lifetimes of carbocations is given.

The first systematic studies on the kinetics of the reactions of carbocations with nucleophiles were performed by Ritchie[5] who investigated the reactions of highly stable carbocations, such as tritylium and tropylium ions with anions and amines. This work has largely been extended by Jencks and Richard [6] by introducing the *azide clock* method. The method is based on the fact that many carbocations react with the azide ion with a known diffusion-controlled rate constant of $5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$. One allows two nucleophiles to compete for the intermediate cation, R^+ produced under solvolytic condition. The first nucleophile is the azide ion (N_3^-) and the other is the solvent (SOH). Then as the rate constant for reaction with azide is known, the product ratio $[\text{RN}_3]/[\text{ROH}]$ can be used to calculate the rate constant of the reaction of R^+ with the solvent SOH. This is known as the 'competition kinetic technique'. Further, if the compound selected for generation of the carbocation contains an azide leaving group, the use of azide-clock experiment is much simpler and a simple UV-Vis spectrophotometer is enough to carry out the experiment. In the following we consider the determination of lifetimes of α -azido benzyl carbocation and α -(2,2,2)-trifluoro ethoxy benzyl carbocation using this method.

Solvolysis rate constants for the reaction of the benzyl-*gem*-diazides [7] or α -azido benzyl (2,2,2)-trifluoroethyl ether [8] in water containing 1% acetonitrile at 25°C and at a constant ionic strength of 2.0 M, maintained with NaClO_4 can be determined using the following procedure. The solvolysis reaction can be initiated by making a 100-fold dilution of a solution of the substrate in acetonitrile to give a



Scheme 2.

final concentration of 1.0×10^{-4} M (for example, injecting 30 μL of the stock solution of the substrate in acetonitrile into 3 mL of 2M solution of NaClO_4 in water, contained in a quartz cell of 1 cm path length). The kinetics can be followed spectrophotometrically by monitoring the appearance of corresponding benzaldehyde or the disappearance of the reactant at their λ_{max} .

The rate of production of the carbocation is given by

$$\frac{d[\text{R}^+]}{dt} = k_{\text{solv}}[\text{RN}_3] - k_{\text{az}}[\text{N}_3^-][\text{R}^+] - k_{\text{H}_2\text{O}}[\text{R}^+].$$

As the carbocation is a very reactive species, one can apply the steady state approximation. Thus putting $d[\text{R}^+]/dt = 0$ and solving this equation for $[\text{R}^+]$ gives

$$[\text{R}^+] = \frac{k_{\text{solv}}[\text{RN}_3]}{k_{\text{az}}[\text{N}_3^-] + k_{\text{H}_2\text{O}}}. \quad (1)$$

Since rate of production of RCHO is given by

$$\frac{d[\text{RCHO}]}{dt} = k_{\text{H}_2\text{O}}[\text{R}^+],$$

one gets

$$\frac{1}{[\text{RN}_3]} \frac{d[\text{RCHO}]}{dt} = k_{\text{obsd}} = \frac{k_{\text{solv}}k_{\text{H}_2\text{O}}}{k_{\text{az}}[\text{N}_3^-] + k_{\text{H}_2\text{O}}}. \quad (2)$$

The lifetime of the cation is defined as the reciprocal of the rate constant $k_{\text{H}_2\text{O}}$.

Here k_{obsd} is the experimentally determined first-order rate constant for the appearance of the product or for the disappearance of the reactant in the presence of the added azide ion. It would be equal to k_{solv} in the absence of the added azide ion. Taking the reciprocal of equation (2) we get

$$\frac{1}{k_{\text{obsd}}} = \left(\frac{k_{\text{az}}}{k_{\text{H}_2\text{O}}} \right) \left(\frac{1}{k_{\text{solv}}} \right) [\text{N}_3^-] + \frac{1}{k_{\text{solv}}} \quad (3)$$

or

$$\frac{k_{\text{solv}}}{k_{\text{obsd}}} = \left(\frac{k_{\text{az}}}{k_{\text{H}_2\text{O}}} \right) [\text{N}_3^-] + 1. \quad (4)$$

So in a plot of $k_{\text{solv}}/k_{\text{obsd}}$ vs. $[\text{N}_3^-]$ (see Figure 1 and Table 1), the slope gives the ratio $k_{\text{az}}/k_{\text{H}_2\text{O}}$. From the literature value of k_{az} ($5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$, Steenken *et al.* [3]), $k_{\text{H}_2\text{O}}$ the rate constant for the disappearance of the cation with solvent could be calculated. The reciprocal of $k_{\text{H}_2\text{O}}$ is the lifetime of the cation. In the present work, from the plot the slope was found to be 450 M^{-1} . This gives a value

Dependence of $k_{\text{solv}}/k_{\text{obsd}}$ on the concentration of added azide ion for the solvolysis of 4-methylbenzyl-gem-diazide in water at 25 °C, and in 2.0 M NaClO_4

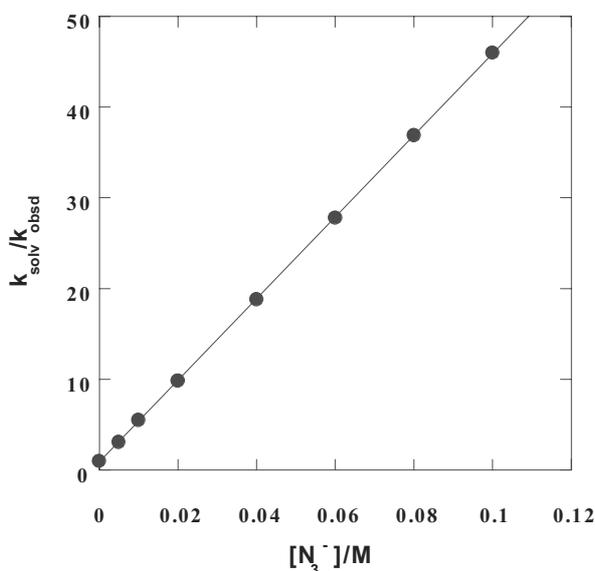


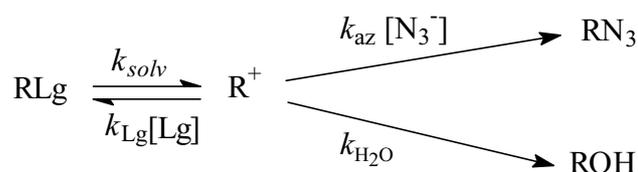
Figure 1. This graph is plotted using the data from Table 1 and equation (4). The slope is equal to $(k_{\text{az}}/k_{\text{H}_2\text{O}}) = 450 \text{ M}^{-1}$. Using k_{az} ($5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), the value of $k_{\text{H}_2\text{O}}$ was found to be $1.1 \times 10^7 \text{ s}^{-1}$. The reciprocal of $k_{\text{H}_2\text{O}}$ gives the lifetime of the cation as 91 ns.

$[\text{N}_3^-]/\text{M}$	$k_{\text{obsd}} \times 10^4/\text{sec}$	$k_{\text{solv}}/k_{\text{obsd}}$
0.00	66.1	1.00
0.005	21.3	3.10
0.01	12.1	5.48
0.02	6.71	9.85
0.04	3.52	18.8
0.06	2.38	27.8
0.08	1.79	36.9
0.1	1.36	48.5

Table 1. Dependence of $k_{\text{solv}}/k_{\text{obsd}}$ on the added azide ion concentration for the solvolysis of 4-methylbenzyl-gem-diazide in water at 25°C and in 2.00 M NaClO_4 .

of $k_{\text{H}_2\text{O}}$ equal to $1.1 \times 10^7 \text{ s}^{-1}$, the reciprocal of which gives the lifetime of the cation as 91 ns.

If the rate constant data for the leaving group (Lg) with carbocation is not available from direct measurements, then the solvolysis experiments should be carried out in presence of the added azide ion. Now the azide ion and the solvent compete for the carbocation together with the Lg. However one is not interested in the rate constant for reaction of the leaving group with the cation. Therefore a rate law can be derived for the following mechanism:



$$\frac{[\text{RN}_3]}{[\text{ROH}]} = \frac{k_{\text{az}}[\text{N}_3^-]}{k_{\text{H}_2\text{O}}}$$

where $[\text{RN}_3]/[\text{ROH}]$ is the ratio of the azide and solvent adducts with the cation, which can be determined using HPLC. k_{az} is the rate constant of the reaction of azide ion with the carbocation which is again equal to $5 \times 10^9 \text{ mol}^{-1} \text{ sec}^{-1}$. Hence, $k_{\text{H}_2\text{O}}$, the rate constant for the collapse of the cation with solvent can be obtained, the reciprocal

The (4-methylphenyl) azidomethyl cation has a lifetime of 91 nanoseconds.

of which gives the lifetime of the carbocation. Several of these rate constants are reported by the author [6–8] and also from our laboratory [9].

The method suggested is quite simple and is easy to carry out in an undergraduate laboratory.

Suggested Reading

- [1] H Meerwein, K Van Emster and J Jousen, *Ber.*, Vol.55B, pp.2500-28, 1922.
- [2] S P McManus and C U Pittman Jr, 'Carbonium ions' in *Organic reactive intermediates* edited by Samuel P McManus, Academic Press, New York, 1973.
- [3] Robert A McClelland, V M Kanagasabapathy, Narinder S Banait and S Steenken, *Journal of the American Chemical Society*, Vol.113, pp.1009-14, 1991.
- [4] M Eigen and E M Eyring, *J. Am. Chem. Soc.*, Vol.84, p.3254, 1962.
- [5] (a) Calvin D Ritchie, *Accounts of Chemical Research*, Vol.5, pp.348-54, 1972.
(b) Calvin D Ritchie, *Canadian Journal of Chemistry*, Vol.64, pp.2239-50, 1986.
- [6] a) John P Richard and William P Jencks, *Journal of the American Chemical Society*, Vol.104, pp.4689-91, 1982.
b) John P Richard and William P Jencks, *Journal of the American Chemical Society*, Vol.104, pp.4691-2, 1982.
- [7] John P Richard, Tina L Amyes, V Jagannadham, Lee Yong-Gu and Douglas J Rice, *Journal of the American Chemical Society*, Vol.117, pp.5198-205, 1995.
- [8] V Jagannadham, Tina L Amyes and John P Richard, *Journal of the American Chemical Society*, Vol.115, pp.8465-6, 1993.
- [9] R Sanjeev and V Jagannadham, *Proc. Indian Acad. Sci. (Chem. Sci.)*, Vol.114, p.47, 2002.

