

Bimolecular Reactions on a Timescale below 1 ps

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Abstract: Access to the intrinsic reaction rate is gained by canceling out diffusion. The use of precursors on demand and reactive solvents allows the study of reactions down to 220 fs. Even the molecular rotation is considerably slower and a preformed, favorable configuration is concluded.

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1. Beating diffusion to get access to the intrinsic rates of bimolecular reactions

Chemical reactions in solution are thought to be limited by the diffusive approach of the reaction partners. Even for reactions that occur on the first encounter, the observed reaction time cannot be faster than several nanoseconds [1]. This so-called diffusion limit masks the intrinsic reaction rate and allows no direct insight into the specific reaction mechanism. To overcome this limitation we use one reactant as the solvent. Therefore it is already in close vicinity to the solute chosen to react with. The second condition to be met is the activation of one of the reaction partners on demand in order to be able to synchronize the reaction and the observation.

The reaction we study is a nucleophilic substitution reaction of benzhydryl chloride. The precursor undergoes photolysis to produce a benzhydryl cation. In this way, the reaction can be triggered by light excitation to produce the cation on demand and it is free to react right away with a proper nucleophilic partner. Using the nucleophilic reaction partner as solvent cancels the need for a diffusional approach and allows for direct observation of the intrinsic reaction rate. The reaction time is now only dependent on the reactivity and on the orientation of the involved molecules. In our measurements we find time constants down to 220 fs for the most reactive combinations. This is three orders of magnitude faster than the diffusion limit and faster than all bimolecular reactions observed up to now. Surprisingly, it is also at least one order of magnitude faster than the rotational relaxation times of the nucleophiles and at the timescale of molecular vibrations.

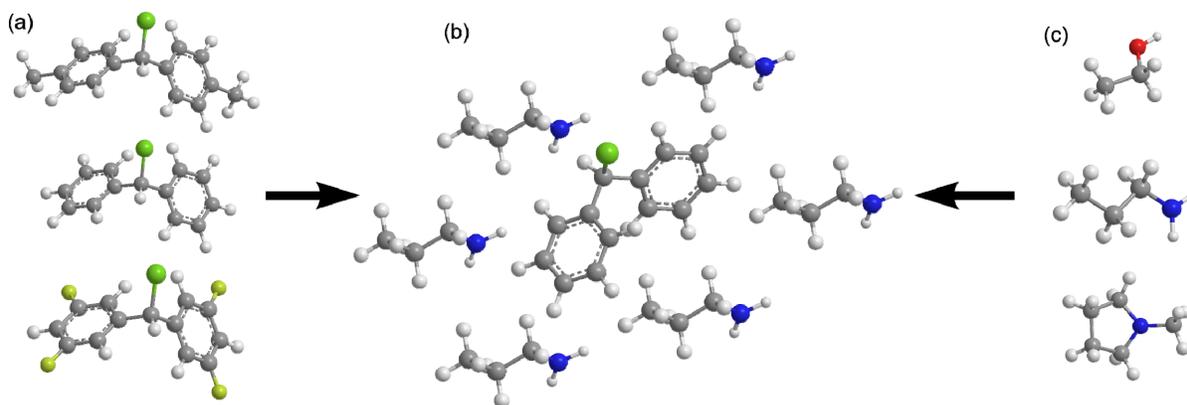


Fig. 1. (a) Benzhydryl chloride (B-Cl, middle) precursor with methyl (B-Me2-Cl, top) and fluorine substitution (B-F4-Cl, bottom). (b) Reaction mixture of precursor and nucleophilic solvent. (c) Strong nucleophiles: Ethanol, n-propylamine and N-methylpyrrolidine (from top to bottom).

2. Tuning reactivity to speed up reaction times

We perform femtosecond pump-probe measurements with a 30 fs pump pulse at 270 nm and a supercontinuum probe pulse ranging from 290 to 720 nm. With this setup we can follow the reaction of the benzhydryl cations with a time resolution of about 50 fs. The benzhydryl compounds are well established reference electrophiles in nucleophilic substitution reactions. The photoexcitation of benzhydryl chloride leads to the cleavage of the carbon-chlorine bond. The bond can cleave either homolytically or heterolytically resulting in a benzhydryl cation and a chlorine anion or in the corresponding radical pair. A rapid removal of the chlorine in 125 fs leads to the cation [2]. The reaction of the cation with the nucleophile can be followed by the decay of its unique spectral signature around 440 nm [2,3]. The decays of the cation signal shown in Fig. 2 demonstrate that we can follow extremely fast

reactions that depend strongly on the individual pair of reactants. By chemical analysis we confirm that the decreasing cation population is indeed due to the bimolecular reaction.

We tune the reactivity of the cation by substitution on the phenyl rings. Substitution of electron withdrawing fluorine makes the cation much more reactive while an electron donating methyl substitution leads to longer reaction times. Additionally, we choose a variety of different alcohols and amines as nucleophiles to react with the benzhydryl cations. For the alcohols we can adjust the reactivity mainly by the carbohydrate chain length. For methanol we measure reaction times from 200 ps down to 2.6 ps (Fig. 2a-b). This is on the edge of rotational relaxation times for small molecules. Even higher reaction rates are achieved with amines ranging from a few ps down to 200 fs (Fig. 2c).

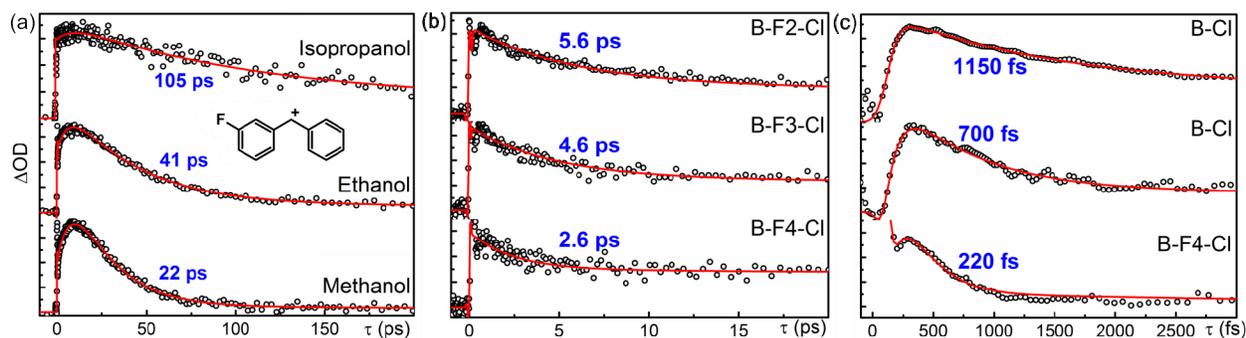


Fig. 2. Experimental results for the decay of the cation spectral signature at 440 nm. (a) Time traces and fits of the cation signal for alcohols with decreasing chain length. (b) Time constants for methanol reach the rotational limit. (c) For amines the reactions are even faster. Shown are examples of the cation trace for diaminopropane (top), *N*-methylpyrrolidine (middle) and *n*-propylamine (bottom).

For the amines we can reach higher reactivities by going from primary to tertiary amines. Remarkably, chemical variation loses its effect for the fastest reactions (Table 1). A typical rotational relaxation time for molecules of this size is 20 ps. This means the molecule cannot fully rotate before the reaction appears. Therefore the orientation of the molecules has to fit a certain angle and distance to make the extremely fast reaction possible. They have to be in the right orientation already before the light induced bond cleavage. Intermolecular interactions seem to play a crucial role here because precursor and nucleophiles both can form hydrogen bonds to bring the reactants into the favorable configuration. This has also been suggested by molecular dynamics simulations [3].

Table 1: Time constants for the reaction of the cation. In the nomenclature of the precursor mainly the substitution of the used benzhydryl chlorides (B-Cl) is marked by Me (methyl) or F (fluorine). All time constants in ps.

Precursor	Ethanol	Methanol	Propyl-amine	Butyl-amine	Diamino-propane	Pyrro-lidine	<i>N</i> -methyl-pyrrolidine
B-Me2-Cl	239	203	3.1	2.5	2.3	1.6	1.6
B-Me-Cl	103	76	2.5	1.6	2.4	1.0	1.1
B-Cl	56	32	1.65	1.21	1.15	0.73	0.71
B-F-Cl	41	22	0.84	0.75	0.72	0.61	0.48
B-F2-Cl	-	5.6	0.57	0.60	0.45	0.49	0.25
B-F3-Cl	-	4.6	0.31	0.34	0.38	0.30	0.24
B-F4-Cl	-	2.6	0.22	0.26	0.26	0.26	0.22

The observation of the bimolecular reaction of a reactant produced on demand by photolysis and a surrounding partner allows the determination of the intrinsic reaction speed. It is found to be faster than even the rotational relaxation time. The reaction happens nearly immediately on the first vibrational encounter and the highly reactive species already have a favorable orientation before photolysis.

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