t_2^{\dagger}

t‡

t₀

Femtosecond Nucleophilic Substitution Reaction **Dynamics**

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A general class of reactions termed aromatic nucleophilic substitution (S_NAr) is central to organic syntheses, reaction mechanisms, and electron transfer processes.¹ A textbook example is the following reaction which is generally considered



as a two-step process, the addition of the nucleophile $(a \rightarrow b)$ and the elimination to form final products ($b \rightarrow c$). However, if the processes of addition and elimination are concerted, the so-called σ -complex (b) becomes a transition state, similar in nature to S_N2 reactions.²

The dynamics of this elementary nucleophilic process is of great interest for a number of reasons. First, the potential energy surface³ defines regions of transition states and complex intermediates, and these intermediates have been the subject of many experimental studies.⁴ Second, the process involves both electronic and nuclear rearrangements, and these occur on the femtosecond to picosecond time scale, hitherto unresolved. Third, the true lifetime of the intermediate determines the exact mechanism for the addition and elimination and reflects the nature of energy redistribution, statistical or not.4a,5

In this paper, we present our first study of S_NAr reactions with femtosecond resolution. The system of particular interest here is the reaction of a chlorine atom anion (Cl⁻, nucleophile) with an iodobenzene cation (IBz⁺, substrate) to form product chlorobenzene and iodine. The concept of the experiment can be described as follows. In a molecular beam, a femtosecond pulse is used at t = 0 to create the charge separation in the van der Waals IBz·Cl₂ complex. In this way, the transition state region, where the reagents are angstroms apart, is directly entered,⁶ and because of the limited impact parameters, the barrier is minimally governed by centrifugal effects. The Cl2⁻ is formed above the dissociation limit⁷ and breaks up, leaving the Cl^- to attack the most electron-deficient *i*-carbon of the

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Figure 1. Five snapshots of schematic structures to illustrate the preparation and evolution of the nucleophilic substitution reaction. Emphasis is on the structural change prior to the femtosecond preparation (t_{-}) , when separation of charges occurs (t_{0}) , in the transition state region $(t_1^{\ddagger}, t_2^{\ddagger})$ and for final products (t_f) . The initial structure is assumed in analogy with Bz/X₂ systems.^{6b} The energetics and reaction path are shown in the insert,10 and the initial wave packet in the transition state region is displayed at the available energy. Note that for the neutral Cl + IBz reaction, the collision energy will be less than the \sim 35 kcal/mol value (\sim 10 kcal/mol) because of Cl₂ direct dissociation.

cation.⁸ Hence, a σ -complex can be formed but in contrast to b in eq 1, in this case, it is a delocalized i-cyclohexadienyl radical.⁹ The activated σ -complex is probed with a second femtosecond pulse by monitoring in time the liberated I atom and the kinetic energy-resolved time-of-flight (KETOF) distribution. The reaction steps are illustrated in Figure 110 and details of the apparatus can be found elsewhere.⁶

As shown in Figure 2, the mass spectra and KETOF distributions clearly show features of the reaction products. Without Cl₂ in the beam, only two peaks (>15 μ s) of IBz⁺ and I^+ appear in the mass spectrum. With a controlled concentration of Cl₂, a large enhancement of the I⁺ signal and two new mass peaks, ClBz⁺ and IBzCl⁺, becomes evident. This enhancement is from the charge transfer (CT) initiation at $t = 0.6^{6}$ Indeed,

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⁽¹⁰⁾ The σ -complex energetics is estimated by considering the exothermic addition of Cl atom to a carbon double bond (-21 kcal/mol¹¹) and an endothermic disruption of the π -electron framework of the ring (resonance stabilization energy, 11 kcal/mol).¹² This places the σ -complex below the Cl + IBz by -10 kcal/mol and the products, ClBz + I, by -30 kcal/mol (exothermic). There may be a small barrier for the σ -complex to decompose into the products. The ionic state (IBz⁺Cl⁻) is estimated to be ~30 kcal/ mol above the Cl + IBz, and the total available energy for the σ -complex is \sim 45 kcal/mol.



Reaction Time (fs)

Figure 2. Upper panel: (left) TOF mass spectra without (dotted) and with (solid line) Cl₂ under the same conditions; (right) the corresponding I⁺ KETOF distributions taken at a ~6 ps delay time (the enhancement of the I⁺ KETOF signal is also shown (heavy solid line)). Lower panel: the experimental fs transient, which is well simulated by a single exponential rise with $\tau = 880$ fs (solid line), obtained by gating the central part of the I⁺ KETOF distribution with 60 ns gate width. The temporal response of the system is also indicated (dashed line). Note that KETOF patterns depend on polarization and aperture arrangement.^{6b,17}

the initial excitation is confirmed to be a one-photon process (277 nm), and the I detection is by the known 2 + 1 resonance enhanced multiphoton ionization (REMPI, 304.6 nm). The product formation of I and the nucleophilic substitution of Clwere consistent with the following observations: (1) as with the Bz·I₂ system,⁶ the CT absorption of the IBz·Cl₂ complex is much larger than that of IBz13 and hence the observed enhancement, even though the total complex concentration is only a few percent of that of IBz, is from the CT excitation; (2) the Cl₂ absorption is very weak at 277 nm,¹⁴ which again is consistent with the minor role of the radical substitution reaction (Cl + IBz); (3) the I⁺ KETOF distributions are very different with and without Cl₂, and the enhanced part is a broad distribution, unlike the typical KETOF distribution observed from iodobenzene.^{15,17} We have also monitored the temporal behavior of reaction constituents IBzCl⁺ and ClBz⁺ to check for consistency with the product I⁺ transient.

We observed (Figure 2) a 880 fs reaction time, orders of magnitude longer than the vibrational periods of the C–I and C–Cl bonds (\sim 60 fs). Since the entrance channel involves Coulombic interaction, the addition process takes place in the

(15) It is known that a new compound of iodobenzene dichloride is formed due to the mixing of Cl_2 with IBz. However, the absorption cross section is similar to IBz.¹⁶ Furthermore, we observed that the enhancement of KETOF disappears when Cl_2 was shut off. If the compound is statically formed in the line, this change will not occur.

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first 100 fs; our MD simulations give 50 fs for the Cl⁻ to approach the IBz⁺ at 2.45 Å separation, similar in magnitude to the result for Cl₂⁻ + Xe⁺.¹⁸ Accordingly, the observed 880 fs reaction time describes the elimination process, a ratedetermining step for a highly nonconcerted reaction. This indicates that a σ -complex is formed during the reaction. Along the one-dimensional reaction path of Figure 1, it is expected that the elimination occurs on the femtosecond time scale if electronic structural changes are controlling the process. However, intramolecular vibrational energy redistribution (IVR) must be involved in determining the effective dimensionality of the potential energy surface (PES)—energy must flow from the site of the nucleophilic attack to the reaction coordinate. Furthermore, steric effects during the attack will slow the rates.

Consistent with the observations are the broad KETOF distributions which indicate vibrational energy involvement in *some* selective modes. In this regard, our results support the theoretical studies of S_N2 reaction lifetimes (multiexponential),^{5a,b} consistent with nonconcerted S_N2 picture,^{5c} and the experimental observation of vibrational excitation in products.^{4a,19} Crossed beam studies of radical substitution reactions have been performed by the Lee and Grice groups.²¹ It is interesting that for F + BzX (X = Br, I), a downhill reaction, the lifetimes of the complexes were deduced to be longer than the rotational period.^{21b} We have also studied other systems, such as the reactions of Br⁻ with IBz⁺ and Cl⁻ with *p*-iodotoluene cation, and obtained similar findings. These results elucidate general features of the approach and these reactions.

The dynamics of the complex reflects the nature of bond making and bond breaking. From a frontier orbital point of view, the interaction of the HOMO of the nucleophile with the σ^* -LUMO of the C–I bond is critical for the formation of final products. Unlike the conventional S_N2 reaction, here the orbitals are orthogonal and with time must change configuration to allow for better interactions. The slower (than electron hybridization) nuclear motions determine the extent of IVR and its influence on the reaction rates. Simple MNDO MO calculations of OH⁻ reaction with *p*-nitrochlorobenzene²² and *ab initio* electronic structure calculations^{8a} of :NH₃ reaction with C₆H₅Cl⁺ support the above picture.

The approach presented here to prepare and study the important nucleophilic substitution reactions is novel in its direct view of the dynamics of the transition state region with minimum impact parameter averaging. There are similar extensions which include studies of other ion-molecule reactions, solvation effects, and different orientations.

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