



Figure 2. Upper panel: (left) TOF mass spectra without (dotted) and with (solid line) Cl_2 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 Cl^- were consistent with the following observations: (1) as with the $\text{Bz}\cdot\text{I}_2$ system,⁶ the CT absorption of the $\text{IBz}\cdot\text{Cl}_2$ complex is much larger than that of IBz ¹³ 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 Cl_2 absorption is very weak at 277 nm,¹⁴ which again is consistent with the minor role of the radical substitution reaction ($\text{Cl} + \text{IBz}$); (3) the I^+ KETOF distributions are very different with and without Cl_2 , 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 (~ 60 fs). Since the entrance channel involves Coulombic interaction, the addition process takes place in the

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 $\text{Cl}_2^- + \text{Xe}^+$.¹⁸ Accordingly, the observed 880 fs reaction time describes the elimination process, a rate-determining 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 $\text{S}_{\text{N}}2$ reaction lifetimes (multiexponential),^{5a,b} consistent with nonconcerted $\text{S}_{\text{N}}2$ 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 $\text{F} + \text{BzX}$ ($\text{X} = \text{Br}, \text{I}$), 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 $\text{S}_{\text{N}}2$ 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 :NH_3 reaction with $\text{C}_6\text{H}_5\text{Cl}^+$ 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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(19) It should be mentioned that after the CT excitation of the $\text{IBz}\cdot\text{Cl}_2$ complex, the back electron transfer could in principle occur to form $\text{IBz}^+\cdot\text{Cl}_2$ or $\text{IBz}\cdot\text{Cl}_2^*$. The $\text{IBz}^+\cdot\text{Cl}_2$ channel is minor based on the observed broad I^+ KETOF distribution.¹⁷ If some trajectories evolve along the other back electron transfer channel ($\text{IBz}\cdot\text{Cl}_2^*$),²⁰ similar to the $\text{Bz}^+\cdot\text{I}_2^-$ system,^{6b} a radical substitution reaction ($\text{IBz}\cdot\text{Cl}$) may occur. The resulting reaction route and dynamics (a slow-step elimination) will be the same as for the $\text{S}_{\text{N}}\text{Ar}$ reaction, as discussed above.

(20) Because there are only fewer repulsive states of Cl_2^* in our energy region, this back electron transfer channel may be less important. For the states of Cl_2 , see: Peyerimhoff, S. D.; Buenker, R. J. *Chem. Phys.* **1981**, *57*, 279.

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(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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