J. Am. Chem. Soc. **1991**, *113*, 9699-9701

complex over that of the low-energy bimolecular collision (~50% vs 1%) is consistent with the transition-state barrier lying below the energy of reactants; that is, a large fraction of the collisionally activated complexes appear to be prepared in an energy range below the entrance channel asymptote and above the transition state. The failure of the exit channel complex [b] to back-react and form Cl^- is anticipated by the high density of states of the Br^- product channel relative to that of the tight transition state for the reaction.

In summary, we have isolated and activated two distinct species captured on the potential energy surface of the gas-phase S_N2 reaction (1). The intermediate corresponding to reactants trapped along the entrance channel reacts to form products with an efficiency of ~50%, far greater than that of the bimolecular reaction, while the intermediate trapped in the exit channel exclusively forms Br^- products upon collisional activation. These results demonstrate the possibility of triggering S_N2 reactions starting from specific configurations along the reactive potential energy surface.

Acknowledgment. We are very grateful to J. L. Wilbur and J. I. Brauman, who graciously offered to include our work along with theirs in joint publication, and to V. H. Wysocki for helpful remarks regarding the energetics of collision-induced dissociation. M.A.J. thanks the National Science Foundation for support of this research.

Registry No. Cl^-, 16887-00-6; Br^-, 24959-67-9; CH_3Cl, 74-87-3; CH_3Br, 74-83-9.

Intermediates and Potential Surfaces of Gas-Phase S_N2 Reactions

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Received August 19, 1991

We report the formation of a putative intermediate in an exothermic gas-phase S_N2 reaction (eq 1) and its induced unimolecular dissociation to both products and reactants. To our knowledge, the isolation and energization of a stable S_N2 intermediate to form products has not previously been reported.[1] This is due in part to the paucity of appropriate systems, which require an internal barrier sufficiently high to allow isolation of the adducts but low enough to accommodate conversion of the intermediate to products. Studies of this type provide direct information about the potential surfaces for gas-phase S_N2 reactions and present the opportunity to evaluate existing models experimentally.

$$CF_3CO_2CH_3 + Cl^- \rightarrow [CF_3CO_2CH_3Cl]^- \rightarrow CF_3CO_2^- + CH_3Cl \quad (1)$$

Nucleophilic displacement reactions have been studied extensively in solution,[2] in the gas phase[3] and by theory.[4] An important goal of these investigations has been to obtain an accurate picture of the potential energy surface for gas-phase S_N2 reactions. The double-minimum potential surface (shown schematically in Figure 1) exhibits two ion-dipole complexes as minima separated by a transition state. Such a surface was first proposed to explain the observation that gas-phase S_N2 reactions can proceed at rates below the collision rate.[3c] Subsequent experimental[3c-q] and theoretical[4h-m,p,q] studies have been consistent with the proposed surface. Complexes corresponding to intermediates in gas-phase S_N2 reactions have been generated[3e,k,5] and shown to be unsymmetrical[3e,5a] but have never been converted successfully to products. In isolating an intermediate and inducing its unimolecular decomposition to products, we provide a missing link in the direct characterization of the topology of the potential surface.

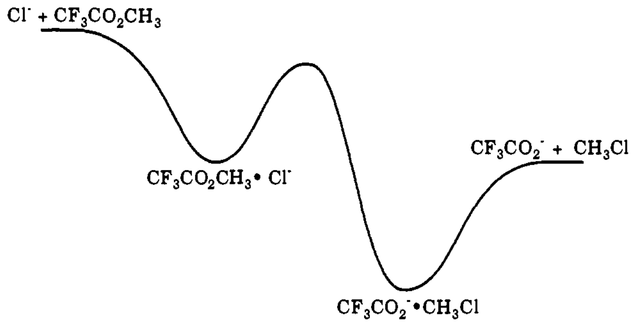

Figure 1. The double-minimum surface for gas-phase S_N2 reaction 1. Minima correspond to complexes bound by electrostatic attractions between the ion and the dipole of the neutral.

All experiments were performed with an IonSpec OMEGA system, equipped with impulse excitation.[6] Other details of the

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Table I. Ratios of Dissociation Products from IR Photolysis of Gas-Phase S_N2 Intermediate

	branching ratio: $CF_3CO_2^-/Cl^-$	efficiency: $CF_3CO_2^-$/total ions	% photo-dissociation
low intensity	4	0.88	5%
high intensity	0.55	0.35	85%
bimolecular reaction	~0.02	0.02	

experimental configuration have been described elsewhere.[7] The creation of stable adducts directly from a bimolecular association reaction requires a collision with a third body to remove excess energy. At ion cyclotron resonance (ICR) pressures (10^{-7} Torr), these third-body collisions rarely occur. Thus, adducts were formed using McMahon's method as shown below.[8] Chloride, generated via electron impact (eq 2), reacts with methyl chloroformate to give the chlorocarbonate anion (eq 3), which then donates chloride to form the desired adduct (eq 4). Activation of the intermediate was accomplished by infrared multiple photon (IRMP) activation,[9] with typical photochemical yields ranging from 5 to 85% at the extremes of low- and high-intensity irradiation,[10] respectively. All IRMP experiments used the output of a pulsed CO_2 TEA laser, which was attenuated to achieve different intensities.

$$ClCO_2CH_3 \xrightarrow{e^-} Cl^- + CO_2CH_3 \qquad (2)$$

$$Cl^- + ClCO_2CH_3 \rightarrow ClCO_2^- + CH_3Cl \qquad (3)$$

$$ClCO_2^- + CF_3CO_2CH_3 \rightarrow CO_2 + CF_3CO_2CH_3{\cdot}Cl^- \qquad (4)$$

The S_N2 reaction (eq 1) is exothermic by 13.5 kcal/mol,[11] yet proceeds at only 2% efficiency,[3e] indicating that some barrier to product formation must exist. The intermediate was sufficiently stable to be isolated and could be energized by IRMP activation. The S_N2 reaction is the only accessible channel for chloride substitution.[12]

Given the exothermicity of reaction 1, and the method of generating the adducts, the most likely structure for the intermediate we have observed is the ion–dipole complex **1A**. This

$$\underset{\textbf{1A}}{[CF_3CO_2CH_3]{\cdot}Cl^-} \qquad \underset{\textbf{1B}}{[CF_3CO_2^-]{\cdot}CH_3Cl}$$

is confirmed by our observation that the isolated intermediate can readily transfer chloride to CF_3H, indicating that the chloride is loosely bound, and ruling out the ion–dipole complex **1B**, in which the methyl group has been transferred. The possibility that the complex **1A** is actually a covalent adduct of Cl^- to the carbonyl group is not ruled out directly by the data presented here but is unlikely based on the behavior of other Cl^- adducts to carbonyl groups, all of which are less stable than the corresponding ion–dipole complexes.[7,13] In addition, chloride-transfer experiments indicate that the stability of the intermediate is comparable to that of other known ion–dipole complexes.

IRMP activation of the adduct resulted[14] in unimolecular dissociation both to products ($CF_3CO_2^-$) and to reactants (Cl^-), indicating that the height of the reaction barrier is within a few kilocalories/mole of the energy of the reactants,[15] consistent with the low efficiency (~2%) determined in kinetic studies. The ratio of the photolysis products formed represents the branching between crossing the reaction barrier to products and returning to reactants through the entrance channel. A comparison of branching ratios, which change as a function of the intensity of the IR laser pulse, is shown in Table I.

The branching ratios, which show mostly product at low intensities and mostly reactant at high intensities, provide details about the potential surface. The barrier to products has a threshold lower than the entrance channel and a rate which increases slowly with internal energy, consistent with a tight transition state. In contrast, the channel leading back to reactants has a higher threshold and a rate which increases rapidly with internal energy, indicating a loose transition state. The demonstration that the intermediate lies in a well between the entrance channel and a reaction barrier (which is at least 11 kcal/mol above the exit channel[16]) is direct evidence for a multiple-well surface, the simplest of which has two wells.

The efficiency of product formation is significantly higher for the photolysis experiments than for the bimolecular reaction (Table I). Because of large impact parameters, the bimolecular reaction is characterized by orbital angular momentum not present in the photolysis experiments. Statistical reaction models were used to determine whether the higher angular momentum in the bimolecular reaction could account for the observed difference in efficiency. The orbital angular momentum in the bimolecular reaction raises the average effective reaction barrier[17] by 2.5 kcal/mol when a fixed value of 8.6 Å is used as the apparent distance between the centers of mass for the association transition state.[18] This value can be compared with more sophisticated RRKM calculations[19] which predict that angular momentum raises the average effective barrier by approximately 1.5 kcal/mol, resulting in an efficiency change which accounts for about 30% of the effects seen. Both calculations indicate that angular momentum plays a significant role in the efficiency of product formation. Differences in energy distributions are also likely to be important. In the energization of an intermediate, there is an energy regime of width 2–3 kcal/mol in which an activated species has sufficient energy to cross the reaction barrier but not enough energy to access the entrance channel.[15,16] For species in this regime, formation of products is unit efficient. In the case of the bimolecular reaction, the reactants have energy at or above both channels. Thus, the intermediate energy range is not accessed and the efficiency is reduced. Details of the energy distributions are not well-known, however, and cannot be treated quantitatively at this time.

In summary, a stable intermediate for a gas-phase S_N2 reaction has been isolated and energized, allowing unimolecular dissociation to products and reactants. These experiments provide direct

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(10) Fluence measurements were taken at the entrance of the ICR cell. A mirror reflects the incident beam back through the ion cloud, resulting in an effective intensity of twice the intensity of the incoming beam. The effective fluence is 2.5–3.0 J/cm^2 at high intensity and 0.5–1.0 J/cm^2 at low intensity, which is twice the measured fluence.

(11) (a) $\Delta H_f^\circ(CF_3CO_2H) - \Delta H_f^\circ(CF_3CO_2CH_3) = -5.2$ kcal/mol (by group additivity: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, NY, 1976). (b) ΔH_f° for Cl^-, CH_3Cl, CF_3CO_2H, and $ClCO_2^-$: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levine, R. D.; Mallard, W. G. *J. Chem. Phys. Ref. Data* **1988**, *17* (Suppl. 1).

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(14) At high fluences, CF_3^- was also observed in small amounts. Changing the laser line to a wavelength which $CF_3CO_2^-$ does not absorb results in no production of CF_3^-, indicating that it is a secondary photoproduct of $CF_3CO_2^-$.

(15) The expected energy range of the energized adducts is about 0–3 kcal/mol (the energy of a 1000-cm^{-1} photon is ~3 kcal/mol) above the barrier for these IRMP activation experiments.

(16) The barrier is 2–3 kcal/mol below the entrance channel (determined by kinetic studies and IRMP activation), and the reaction is exothermic by 13.5 kcal/mol.

(17) $E = (1 - I^{\dagger}/I)k_{BT}$. See: Robinson, P. A.; Holbrook, K. A. *Unimolecular Reactions*; Wiley: London, 1972; pp 88–89.

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information about the topology of the potential surface and show promise as a means of investigating other fundamental reactions.

Acknowledgment. We are grateful to the National Science Foundation for support of this research. We thank Brian Wladkowski for advice and help with the RRKM calculations.

Registry No. $ClCO_2CH_3$, 79-22-1; Cl^-, 16887-00-6; $CF_3CO_2CH_3$, 431-47-0.

Stereoselective Chelation-Controlled Reduction of α-Iodo-β-alkoxy Esters under Radical Conditions[1]

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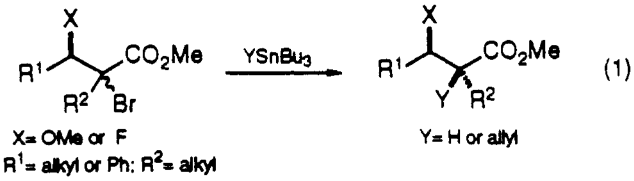
Received August 1, 1991

The application of free-radical reactions in organic synthesis has grown enormously during the past decade providing a wealth of useful new chemistry.[2] However, relatively few reports have addressed the problem of stereocontrol in reactions involving acyclic radicals. Very recently it has been shown that chirality transfer can be achieved successfully using chiral auxiliaries[3] or stereogenic centers adjacent to the radical center.[4,5] In this communication we describe an alternative solution to the problem of stereocontrol in acyclic molecules wherein chelation-controlled reductions are performed under radical conditions.

Previously, we reported that the radical-mediated reduction[5b] or allylation[5c] of acyclic β-methoxy-α-halo or β-fluoro-α-halo esters proceeds with good to excellent stereoselectivity (eq 1). To account for this stereochemical outcome we proposed a transition state as depicted in Scheme Ia.[5b] Consideration of this model led to the hypothesis that a bidentate Lewis acid could alter the structure of the transition state thus changing the stereochemical outcome of the reaction. As shown in Scheme Ib, chelation of the carbonyl and methoxy moieties to a Lewis acid forces the molecule into a conformation which exposes the top face of the radical π system (Newman projection) to hydrogen atom delivery and thus provides access to the erythro manifold.[6]



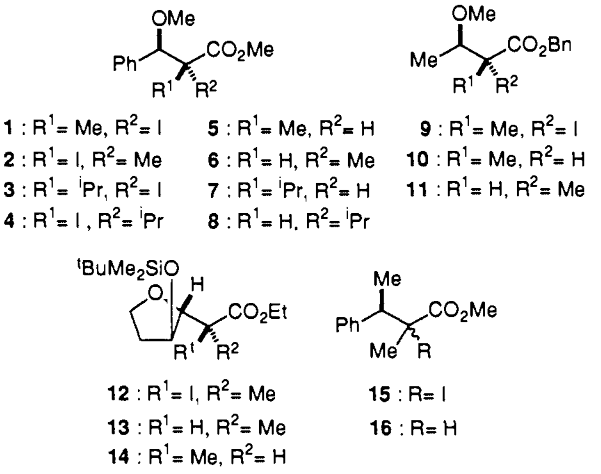


Figure 1.

Scheme I

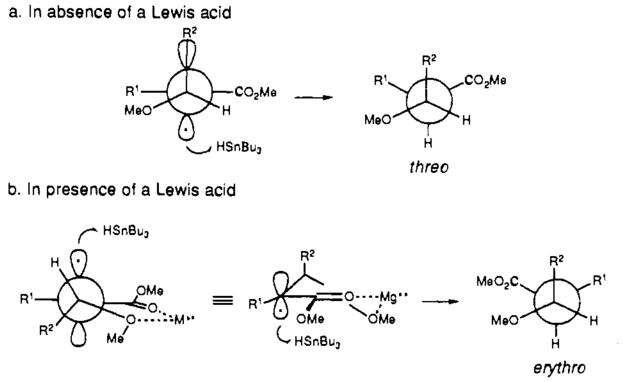


Table I. Reduction of Iodoester **1** with Bu_3SnH in the Presence of Various Lewis Acids

entry	Lewis acid	equiv	ratio[a] (erythro:threo)	yield, %
1			1:>25	90
2	MgI_2	1.0	>25:1	78
3	MgI_2	0.25	25:1	71
4	$MgBr_2{\cdot}OEt_2$	1.0	>25:1	84
5	$MgBr_2{\cdot}OEt_2$	0.25	>25:1	81
6	$AlCl_3$	1.0	>25:1[b]	75
7	$AlCl_3$	0.24	1:1.8	

[a] Ratios determined by ^1H NMR spectroscopy. [b] Threo diastereomer could not be detected by ^1H NMR spectroscopy.

In order to test this hypothesis, iodo ester **1**[7] was treated with Bu_3SnH in the presence of various Lewis acids. As shown in Table I, excellent erythro selectivities were observed when MgI_2, $MgBr_2$-Et_2O, or $AlCl_3$ were employed (entries 2, 4, and 6).[8-10]

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