Lewis Acid-Promoted Kharasch−Curran Additions: A Competition Kinetics Study of Bromine Atom Transfer Addition of *N*-α-Bromoacetyl-oxazolidinone to 1-Hexene

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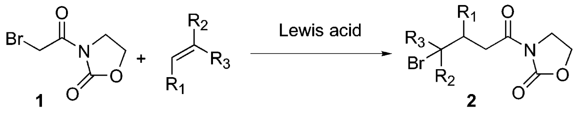
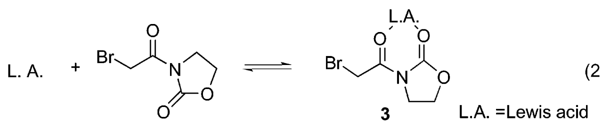
Received March 11, 2002

Lewis acids can efficiently promote free radical atom transfer reactions of an oxazolidinone imide substrate, **1**, derived from α-bromo acetic acid. Thus, **1** undergoes a radical chain addition to 1-hexene giving the atom transfer addition compound, **6**, in the presence of scandium or ytterbium triflate in 1,2-dichloroethane or a cosolvent mixture of 1/9 THF/dichloromethane. In 1,2-dichloroethane the solution is heterogeneous, while the cosolvent mixture gives a homogeneous solution, even at temperatures of −78 °C. Competition experiments were carried out in both solvent systems with added carbon tetrachloride to study how Lewis acid affected the product distribution. In the presence of carbon tetrachloride, chloride **7** is formed in addition to **6** and the ratio of these two products depends on the amount of Lewis acid present. In the presence of ytterbium triflate, in the cosolvent system, the reaction rate of bromine atom transfer was enhanced up to 400-fold compared to the reaction without added Lewis acid. Significant rate enhancements were also obtained in the solvent 1,2-dichloroethane, although the analysis of the system is complicated by the heterogeneous nature of the medium. Computation of C−Br bond dissociation energies (BDE) of the complexed and uncomplexed oxazolidinone bromide suggest that complexation lowers the BDE due to the effect of the strong electron-withdrawing group on the C−Br bond dipole.

There has been a growth of interest in recent years in the utilization of Lewis acids to promote free radical transformations.[1] An advantage of using Lewis acids in radical reactions is the potential to influence the electronic character and reactivity of radicals or alkenes that serve as radical traps. Complexation of Lewis acids to an alkene, for example, promotes the addition of nucleophilic radicals to the alkene, even at low temperatures.[2] In a similar way, a Lewis acid-complexed radical is more reactive with nucleophilic alkenes than is the uncomplexed radical.[3] Lewis acids have also been used to fix the position of stereogenic centers in a reactant or chiral ligand relative to the prostereogenic center of a radical or radical trap undergoing reaction.[3,4] This characteristic has led to significant progress in the use of Lewis acids to promote both diastereoselective and enantioselective free radical transformations.



(1)



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We recently reported that Lewis acids can be used to promote the atom transfer addition of alkyl halides to inactivated carbon−carbon double bonds,[5] a reaction first described by Kharasch[6] and more recently developed into a powerful synthetic sequence by Curran.[7] The transformation we studied is shown in eq 1. In this reaction,

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[1] (a) Nishida, M.; Ueyama, E.; Hayashi, H.; Ohtake, Y.; Yamaura, E.; Yanaginuma, E.; Yonemitsu, O.; Nishida A.; Kawahara, N. *J. Am. Chem. Soc.* **1994**, *116*, 6455−6466. (b) Udding, J. H.; Tuijp, C.; Hiemstra, H.; Speckamp, W. N. *J. Chem. Soc., Perkin Trans. 2* **1992**, 857−858. (c) Guindon, Y.; Yoakim, C.; Lemieux, R.; Boisvert, L.; Delorme, D.; Lavallee, J.-F., *Tetrahedron Lett.* **1990**, *31*, 2845−2848. (d) Guindon, Y.; Lavallee, J.-F.; Llinas-Brunet, M.; Horner, G.; Rancourt, J. *J. Am. Chem. Soc.* **1991**, *113*, 9701−9702. (e) Waldner, A.; De Mesmaeker, A.; Hoffmann, P.; Mindt, T.; Winkler, T. *Synlett* **1991**, 101−104. (f) Renaud, P.; Ribezzo, M. *J. Am. Chem. Soc.* **1991**, *113*, 7803−7805. (g) Renaud, P.; Moufid, N.; Kuo, L. H.; Curran, D. P. *J. Org. Chem.* **1994**, *59*, 3547−3551. (h) Sibi, M. P.; Ji, J. *J. Org. Chem.* **1996**, *61*, 6090−6091. (i) Sibi, M. P.; Ji, J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 190−191. (j) Yamamoto, Y.; Onuki, S.; Yumoto, M.; Asao, N. *J. Am. Chem. Soc.* **1994**, *116*, 421−422. (k) For an excellent review of Lewis acid-promoted free radical reactions, see: Renaud, P.; Gerster, M. *Angew. Chem.* **1998**, *38*, 2562−2579.

[2] Urabe, H.; Yamashita, K.; Suzuki, K.; Kobayashi, K.; Sato, F. *J. Org. Chem.* **1995**, *60*, 3576−3577.

[3] Wu, J. H.; Radinov, R.; Porter, N. A. *J. Am. Chem. Soc.* **1995**, *117*, 11029−11030.

[4] (a) Murakata, M.; Jono, T.; Mizuno, Y.; Hoshino, O. *J. Am. Chem. Soc.* **1997**, *119*, 11713−11714. (b) Fhal, A.-R.; Renaud, P. *Tetrahedron Lett.* **1997**, *38*, 2661−2664. (c) Sibi, M. P.; Ji, J.; Wu, J. H.; Gürtler, S.; Porter, N. A. *J. Am. Chem. Soc.* **1996**, *118*, 9200−9201.

[5] Mero, C. L.; Porter, N. A. *J. Am. Chem. Soc.* **1999**, *121*, 5155−5160.

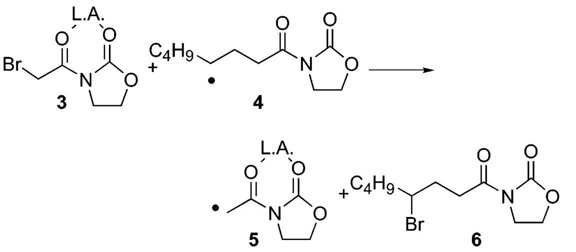
[6] (a) Kharasch, M. S.; Jensen, E. V.; Urry, W. H. *Science* **1945**, *102*, 128−129. (b) For an excellent review, see: Walling, C. *Free Radicals in Solution*; Wiley and Sons: New York, 1957; pp 247−272.

[7] (a) Curran, D. P. *Synthesis* **1988**, 417−39. (b) Curran, D. P. *Synthesis* **1988**, 489−513.

10.1021/jo0201676 CCC: $22.00

β-bromoacyloxazolidinones (the acetyl compound shown here) undergo atom transfer addition to alkenes in the presence of $Yb(OTf)_3$ and $Sc(OTf)_3$. In the absence of Lewis acid, the yield is low or the reaction does not proceed.

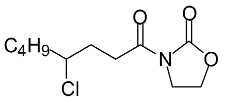
The two propagating steps of the sequence involve addition of the Lewis acid-complexed α-acyl radical, **5**, to the alkene and transfer of bromine to the chain carrying radical from the bromide **1** or its Lewis acid complex, **3**. Lewis acid may have an activating effect on both of the chain-propagating steps in the sequence. Indeed, there is much evidence to support the notion that Lewis acids can be used to promote radical addition reactions,[8] but there is little evidence of the effect of Lewis acids on atom transfer processes. We report here that $Yb(OTf)_3$ and $Sc(OTf)_3$ play a significant role in promoting the reaction described in eq 3. We suggest that complexes such as **3** have enhanced reactivity as bromine atom donors compared to the corresponding uncomplexed bromide **1**.



(3)

Results

We chose to study competition reactions in which the bromide Lewis acid complex **3** and carbon tetrachloride compete for reaction with radical **4**. Thus, when reactions of **1** and 1-hexene were carried out in the presence of carbon tetrachloride, three new products in addition to the bromide **6** were formed. These products, which were isolated and completely characterized, proved to be **7**, the chloro-analogue of **6**, and the addition products to 1-hexene of carbon tetrachloride (1,1,1,3-tetrachloroheptane) **8** and bromotrichloromethane (3-bromo-1,1,1-trichloroheptane) **9**.[9] The chloride **7** is formed by chlorine atom transfer from carbon tetrachloride to the complexed radical **5**. All of the reactions described here for **1** and 1-hexene in the presence of carbon tetrachloride were carried out with a 5-fold excess of the alkene. Reactions with equivalent amounts of alkene and **1** gave good product yields and comparable distribution between products **6** and **7**, but reactions with excess alkene tended to give cleaner product mixtures having fewer minor impurity side products as determined by capillary gas chromatography of the reaction mixtures.



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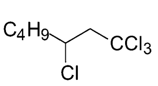

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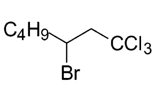

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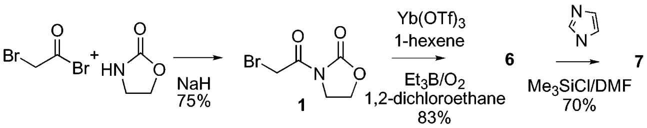
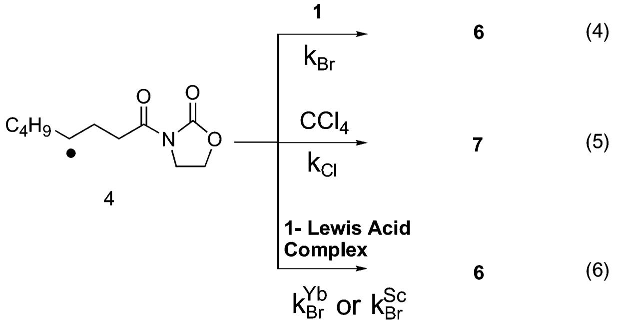
Competition reactions were monitored by gas chromatography, and product ratios of **6** and **7** were determined by an internal standard method. To obtain the pure compounds for preparing standard solutions, oxazolidinones **1**, **6**, and **7** were synthesized as illustrated in Scheme 1. 2-Oxazolidinone was treated with sodium hydride and bromoacetylbromide to give the new oxazolidinone **1** (75% yield),[10] which could be readily converted to bromide **6** in 83% isolated yield by the Lewis acid-promoted addition method.[2] The resulting product **6** could be further transformed into chloride **7** in good yield by reaction with imidazole and trimethylsilyl chloride.

SCHEME 1



SCHEME 2



The ratio of products, **6**:**7**, represents competition of the three pathways shown in Scheme 2, eqs 4−6. By carrying out the competition reaction to less than 10% conversion of starting materials and by analyzing the product mixture of bromide to chloride, **6**:**7**, we determined the effect of Lewis acid on the transformations described by eqs 4−6. To establish a baseline for the competition in the absence of Lewis acid, a series of reactions of **1**, 1-hexene, and carbon tetrachloride were carried out at room temperature with [**1**] = 0.011 M and five different concentrations of carbon tetrachloride, $[CCl_4]$ = 0.002, 0.004, 0.006, 0.008, and 0.011 M). The **6**:**7** product ratios obtained (1.49, 0.77, 0.57, 0.34, and 0.29, respectively) in these experiments permitted the determination of a room-temperature competition constant, $k_{Br}/k_{Cl} = 0.28 \pm 0.04$, for the competition described by eqs 4 and 5.

Reactions of the bromide **1** and 1-hexene, in the presence of the Lewis acids $Yb(OTf)_3$ and $Sc(OTf)_3$ in solvents 1,2-dichloroethane and ether, gave rapid (30 min) and clean conversion to the product **6**. Dichloromethane gave clean product mixtures but slower conversion, while THF, ethyl acetate, benzene, and acetonitrile gave little or no conversion to products. The solubility of the starting bromide **1** and Lewis acid appeared to have a significant effect on the reactions. Solvents that completely dissolved both the starting bromide and the Lewis acid (THF, ethyl acetate, acetonitrile) gave low product yields. Benzene dissolved nei-

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[8] Guindon, Y.; Guerin, B.; Rancourt, J.; Chabot, C.; Mackintosh, N.; Ogilvie, W. W. *Pure Appl. Chem.* **1996**, *68*, 89−96.

[9] The two compounds are formed by addition of a trichloromethyl radical to 1-hexene followed by chlorine atom tranfer from carbon tetrachloride or bromine atom transfer from **1**; see ref 3.

[10] Narasaka, K.; Shimada, S.; Yamada, J.; Hayashi, Y. *Isr. J. Chem.* **1991**, *31*, 261−266.

TABLE 1. Product Ratios of 6:7 for the Reaction of Bromide 1 with 1-Hexene in 1,2-Dichloroethane at Room Temperature as a Function of [Sc(OTf)$_3$][a]

[Sc(OTf)$_3$], M	product ratio (**6**:**7**)
0.000	0.012
0.003	0.017
0.006	0.71
0.008	2.01
0.011	4.07
0.014	4.62
0.017	5.18
0.020	5.18
0.022	5.16

[a] Concentrations of **1** = 0.011 M, 1-hexene = 0.055 M, and CCl_4 = 0.198 M.

ther starting bromide nor Lewis acid, and poor conversion was observed. Although neither $Yb(OTf)_3$ nor $Sc(OTf)_3$ was soluble by itself in 1,2-dichloromethane or ether, addition of the bromide starting material did partially dissolve some, but not all, of the Lewis acids. When the cosolvent system of 1/9 THF/dichloromethane was used in the experiments with varying amounts of Lewis acid, not only was the reaction completely homogeneous but also good conversions were observed for the bromine atom transfer reactions. The reactions promoted by Lewis acids were initiated with 0.1–0.5 equiv of triethylborane/oxygen,[11] and the product mixtures were very clean, with only trace amounts of byproducts being formed.

Reaction of bromide **1** (0.011 M), 1-hexene (0.055 M), and carbon tetrachloride (0.011 M) in the presence of greater than 0.5 equiv of scandium or ytterbium triflate in 1,2-dichloroethane or dichloromethane gave only trace amounts of the product chloride **7**. Under these conditions, the product mixture contains bromide **6** exclusively. Only by increasing the concentration of carbon tetrachloride in these reactions to 10–20 equiv with respect to bromide **1** did we observe product mixtures containing measurable amounts of product chloride **7**. Under these conditions of excess CCl_4 (0.198 M) with respect to **1** (0.011 M), a series of experiments were carried out varying the concentration of scandium triflate from 0.003 to 0.022 M. An internal standard of naphthalene was added to the reaction mixture, and the product halides, **6** and **7**, were analyzed by gas chromatography on an SPB-1 fused silica capillary column. The results of this systematic study are presented in Table 1.

The competition reaction was carried out to a low conversion in the solubilizing cosolvent system (1/9 THF/CH_2Cl_2) at concentrations of CCl_4 = 0.049 M, **1** = 0.022 M, and 1-hexene = 0.112 M. The results of this competition as a function of variable amounts of ytterbium triflate are shown in Table 2. Tridecane was used as an internal standard in this solvent mixture. Triplicate experiments at six different concentrations of Lewis acid were carried out.

TABLE 2. Product Ratios of 6:7 for the Reaction of Bromide 1 with 1-Hexene in 1:9 THF/Dichloromethane at Room Temperature as a Function of [Yb(OTf)$_3$][a]

[Yb(OTf)$_3$], M	product ratio (**6**:**7**)	[Yb(OTf)$_3$], M	product ratio (**6**:**7**)
0.000	0.125	0.0165	35.9
0.000	0.083	0.022	45.6
0.000	0.10	0.022	44.8
0.0055	15.7	0.022	43.8
0.0055	16.3	0.033	50.0
0.0055	16.8	0.033	49.4
0.011	28.5	0.033	49.8
0.011	27.0	0.044	49.8
0.011	29.4	0.044	50.2
0.0165	35.6	0.044	49.1
0.0165	35.1		

[a] Concentrations of **1** = 0.022 M, 1-hexene = 0.110 M, and CCl_4 = 0.049 M.

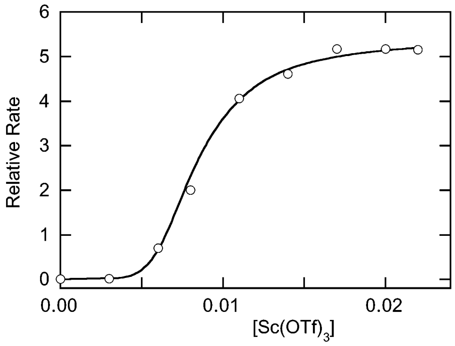

FIGURE 1. Product ratios of **6**:**7** for the reaction of **1** (0.011 mol/L) with 1-hexene (0.055 mol/L) and CCl_4 (0.198 M) in 1,2-dichloroethane at room temperature as a function of added $Sc(OTf)_3$ (mol/L). The smooth curve represents the results of a nonlinear least-squares fit to the two-stage complexation model, eq 8, giving $K_1 = 2.8 \times 10^5$ L/mol and $K_2 = 1 \times 10^4$ L/mol.

Discussion

Scandium Triflate in 1,2-Dichloroethane. The experiments carried out in 1,2-dichloroethane show a clear dependence of bromine atom transfer leading to product **6** on the scandium triflate concentration. The product ratio **6**:**7** approaches an apparent limiting value of 5.5 ± 0.3 at the highest concentrations of scandium triflate, but the effect of Lewis acid on the transformation is complex. The onset of the effect of Lewis acid on the atom transfer reaction occurs at about 0.005 M, an observation that is inconsistent with a simple pre-equilibrium model involving **1** and scandium triflate. A simple pre-equilibrium model predicts enhanced reactivity of the bromide at the lowest concentrations of Lewis acid utilized.[12]

The saturation-limited product ratio observed in Figure 1 provides evidence about the Lewis acid enhancement of bromine atom transfer from **1** to radical **4** in 1,2-dichloroethane. The threshold for onset of catalysis is roughly at $[Sc^{3+}]_0 = [\mathbf{1}]_0/2$, where the subscript 0 indicates the initial concentration prior to reaction. These data can be interpreted in terms of catalysis by a 1:1 complex of Lewis acid and **1** as described in eq 7, but the analysis of data and the curve fit shown in Figure 1 require the additional assumption that a catalytically inactive 2:1 complex of **1**–$Sc(OTf)_3$ forms preferentially at high $[\mathbf{1}]_0$/

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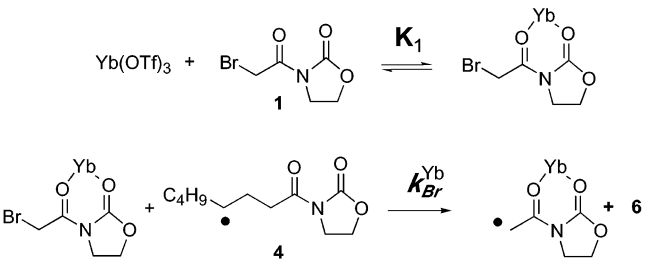
(11) Ollivier, C.; Renaud, P. *Chem. Rev.* **2001**, *101*, 3415–3434.

(12) For an example of the pre-equilibrium model for Lewis acids in free radical chemistry, see the thoughtful analysis in: Ha, C.; Musa, O. M.; Martinez, F. N.; Newcomb, M. *J. Org. Chem.* **1997**, *62*, 2704–2710. The experiments in THF/dichloromethane follow the simple pre-equilibrium model; see Table 2 and Figure 2.

SCHEME 3



$[Sc^{3+}]_0$ ratios (see eq 8). We thus suggest that when $[Sc^{3+}]_0$ is less than 0.5 equiv with respect to **1**, the predominant species present in solution is a 2:1 complex of **1** and the scandium salt. The catalytically active 1:1 complex is present in a substantive amount only if the concentration of scandium triflate is higher than $[\mathbf{1}]_0/2$. Analysis of the data in Figure 1 by a nonlinear least-squares routine based on this two-stage model yields approximate $K_1 = 2.8 \times 10^5$ L/mol and $K_2 = 1 \times 10^4$ L/mol.[13]

$$M^{3+} + \mathbf{1} \rightleftharpoons M(\mathbf{1})^{3+} \qquad K_1 \qquad (7)$$

$$M(\mathbf{1})^{3+} + \mathbf{1} \rightleftharpoons M(\mathbf{1})_2^{3+} \qquad K_2 \qquad (8)$$

We observed cloudiness in the reaction mixtures that led to the data in Figure 1, indicating possible precipitation of some components in the mix. An alternate explanation for the data presented in Table 1 and Figure 1 is that the 1:2 complex of the scandium salt and **1** is insoluble. Attempts to analyze the product dependence with this model gave poorer fits to the data than those obtained by the use of eqs 7 and 8.

Analysis of the data in Figure 1 assumes that the limiting product ratio of **6**:**7** = 5.5 at concentrations over 0.015 M $Sc(OTf)_3$ results from the competition of the reaction of the intermediate radical, **4**, with either a 1:1 complex of **1** and Lewis acid or its reaction with CCl_4. From these data, we calculate that $k_{Br}^{Sc}/k_{Cl} = 99$, which gives a ratio of $k_{Br}^{Sc}/k_{Br} = 355$. Complexation of **1** with $Sc(OTf)_3$ increases its reactivity as a bromine atom donor by a factor of 355.

Competition experiments similar to those described above were carried out with varying amounts of $Yb(OTf)_3$ instead of $Sc(OTf)_3$ added to reactions in 1,2-dichloroethane containing CCl_4 and **1**. The analysis of the effect of ytterbium, while qualitatively similar to that observed for scandium, results in a limiting rate enhancement on bromine atom transfer of $k_{Br}^{Yb}/k_{Br} = 90$, about 25% of the enhancement observed for scandium. Again, cloudy solutions were observed in these experiments.

Ytterbium Triflate in 1/9 THF/CH_2Cl_2. For reactions carried out in 1/9 THF/CH_2Cl_2, the effect of Lewis acid fits the simple model shown in Scheme 3 in which the Lewis acid forms a catalytically active 1:1 complex with **1** with an equilibrium constant K_1. The active reagent in the atom transfer reaction is this complex, which most likely involves not only Lewis acid and **1** but also solvent THF. Analysis of the data in Table 2 by a nonlinear least-squares routine using the simple pre-equilibrium model gives the plot in Figure 2, the value $K_1 = 2 \pm 1 \times 10^3$ L/mol and a rate constant for the competition atom transfer ratio $k_{Br}^{Yb}/k_{Cl} = 115$. From these reactions, the calculated k_{Br}^{Yb}/k_{Br} is determined to be 412.

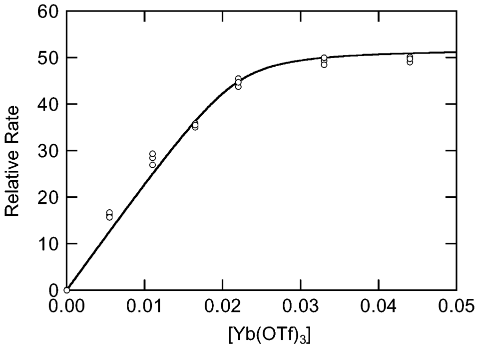


FIGURE 2. Product ratios of **6**:**7** for the reaction of **1** (0.022 mol/L) with 1-hexene (0.112 mol/L) and CCl_4 (0.049 M) at room temperature as a function of added $Yb(OTf)_3$, for reactions carried out in 1:9 THF/dichloromethane. The illustrated points are from three separate runs, and the smooth curve is the result of a nonlinear least-squares fit to the points, which are assumed to track the concentration of the 1:1 complex as predicted by eq 7 with $K_1 = 2 \pm 1 \times 10^3$ L/mol.

Lewis acids have a profound effect on free radical addition reactions, this influence being expressed on both the radical and the alkene undergoing addition.[1,14] The results of this study make clear that Lewis acids can also exert a significant accelerating effect on free radical atom transfer propagation reactions. Assuming that the pre-exponential factor is the same for the catalyzed and uncatalyzed bromine atom transfer implies an effect at room temperature of Lewis acid on the E_a of the catalyzed reaction of approximately −3 kcal/mol compared to the uncatalyzed reaction. Since the critical competition reaction involves rupture of a C−Br bond, it is reasonable to suggest that the acceleration by the Lewis acid is due, at least in part,[15] to weakening of this bond by complexation.

C−Br Bond Dissociation Energies for Lewis Acid Complexes of 1. Recent calculations of carbon−bromine bond strengths have shown[16] that there is a small (ca. 2 kcal/mol) bond-weakening effect of electron-withdrawing substituents on the carbon−bromine bond in para-substituted benzyl bromides. Complexation of a Lewis acid to **1** may have a similar effect on the carbon−bromine bond. To examine this possibility, the C−Br bond dissociation enthalpy (BDE) of **1** was calculated and compared to that in **1** complexed to a proton, a lithium ion, magnesium chloride, and zinc chloride. The results of these computations are presented in Table 3.

The computations suggest that complexation of an electron-withdrawing (EW) species to **1** such as a proton or a Lewis acid results in a weakening of the C−Br bond.

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[13] Despite the good visual agreement in Figure 1, the absolute values of the *K*s are determined only in an order-of-magnitude sense, though their ratio is determined with a precision of ∼40%

[14] . Yang, D.; Gu, S.; Yan, Y. L.; Zhu, N. Y.; Cheung, K. K. *J. Am. Chem. Soc.* **2001**, *123*, 8612−8613

[15] It should be noted that polar effects might also play a role in promoting the atom transfer reaction when Lewis acids are employed. Nucleophilic radicals would be more reactive with electrophilic halo atom donors, and Lewis acids would increase the electrophilic character of the bromide **1**.

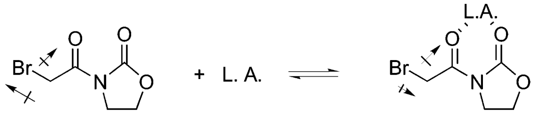
[16] Pratt, D. A.; Wright, J. S.; Ingold, K. U. *J. Am. Chem. Soc.* **1999**, *121*, 489−513.

TABLE 3. Calculated Carbon−Bromine Bond Dissociation Enthalpies (BDEs) of 2-Bromoacetyl-2-oxazolidinone Amides Complexed to Lewis Acids[a]

Lewis acid	LLM[b]	MLM[c]
none	63.1 (0.0), 63.0 (0.0)[e]	63.4 (0.0)
H^+ (toward)[d]	59.0 (−4.1)	59.1 (−4.3)
H^+ (away)[d]	60.0 (−3.1)	60.3 (−3.1)
Li^+	61.2 (−1.9)	60.8 (−2.6)
$ZnCl_2$	62.0 (−1.0)[e]	
$MgCl_2$	62.3 (−0.7)[e]	

[a] Differences from uncomplexed oxazolidinone are given in parentheses. All values are given in kcal/mol. [b] LLM = low-level model = (RO)B3P86/6-311G(d,p)//AM1/AM1. [c] MLM = medium-level model = (RO)B3P86/6-311G(d,p)//MP2(full)/6-31G(d)/HF/6-31G(d). [d] Proton can be positioned closer to either the acetyl carbonyl (toward) or the oxazolidinone carbonyl (away); all other Lewis acids were roughly equidistant from the carbonyl groups. [e] Denotes that PM3 used in place of AM1; AM1 is not parametrized for Zn or Mg.

As originally suggested by Clark and Wayner,[17] the bond-weakening effect of the complexed Lewis acid can be understood by considering that the introduction of the EW group destabilizes the C−Br bond dipole in the parent compound, stabilizing the radical with respect to the parent. Indeed, this is apparent when the charge distributions in the complexes are considered and compared to the uncomplexed bromoacetyl oxazolidinone. Thus, the C−Br bond dipole[18] for **1** changes from +0.07 with no Lewis acid and +0.02 as the $ZnBr_2$ complex to −0.02 with a complexed lithium ion and −0.04 with a complexed proton. We conclude that substitution of strongly electron-withdrawing groups onto a carbon bearing bromine has a dramatic effect on the normal C−Br dipole and also weakens the C−Br bond.



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Atom transfers are among only a few propagation reactions available to free radicals, and as such, they are fundamentally important. Adding a new control element to this fundamentally important reaction type may provide opportunities for introducing selectivity, particularly chemo- and stereoselectivity,[19] to radical transformations in new and interesting ways.

Experimental Section

Bromides **1** and **6** were prepared as previously described.[2] The preparation of **7** started from **6**. Thus, 188 mg of **6** (0.64 mmol) was mixed with imidazole (87 mg, 1.28 mmol) and stirred in DMF (3.2 mL) under nitrogen, and TMSCl (0.11 mL, 0.83 mmol) was added. The reaction mixture was heated at 90 °C for 2 h. After cooling, the reaction mixture was partitioned between hexane and water. The hexane solution was washed with water twice and dried ($MgSO_4$). Evaporation of the solvent afforded the product in 53% yield. Analytically pure product was obtained by flash chromatography on silica gel (2/8 ethyl acetate/hexane): ^1H NMR (400 MHz, $CDCl_3$) δ 4.39 (t, J = 10.8 Hz, 2 H), 3.99 (t, J = 10.8 Hz, 2 H), 3.95 (m, 1 H), 3.13 (t, J = 9.6 Hz, 2 H), 2.13 (t, 1 H), 1.96 (m, 1 H), 1.72 (m, 2 H), 1.50−1.34 (m, 2 H), 1.33−1.29 (m, 2 H), 0.88 (t, J = 7.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 153.5, 62.9, 62.1, 42.5, 38.3, 32.7, 32.3, 28.6, 22.2, 13.9; HRMS calcd for $C_{11}H_{18}ClNO_3$ 247.0975, found 247.0979. Anal. Calcd for $C_{11}H_{18}ClNO_3$: C, 53.33; H, 7.32; Cl, 14.31. Found: C, 53.41; H, 7.10; Cl, 14.38.

General Procedures for Competition Experiments in THF/CH_2Cl_2. A cosolvent solution (5 mL, 1/9 THF/CH_2Cl_2) of **1**[2] (23.4 mg, 0.112 mmol), internal standard tridecane (13.7 μL, 0.056 mmol), and varying amounts of $Yb(OTf)_3$ was stirred at room temperature for 30 min. CCl_4 (24 μL, 0.246 mmol) and 1-hexene (70 μL, 0.56 mmol) were then added subsequently by syringe. The resulting solution was purged with dry air for 5 min and initiated with Et_3B (1 M in hexane) by syringe. The amount of Et_3B varied (usually 0.1−0.5 equiv) depending on the amounts of $Yb(OTf)_3$ used. The reaction was monitored by GC to make sure that the conversions of starting materials were less than 10%. The reaction was quenched with aqueous ammonium chloride and water, and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4 and passed through a short silica gel column. The resulting solution was injected into a GC apparatus to determine the conversions of the starting materials and the product ratio **6**:**7**. A fused silica capillary column (15 m × 0.32 mm × 0.25 μm) was used. The inlet injection T = 150 °C, the FID detector T = 150 °C. The following was the oven program: rate I, from 80 to 120 °C (4 °C/min); rate II, from 120 to 220 °C (5 °C/min), final time = 2 min; rate III, from 220 to 280 °C (20 °C/min), final time = 5 min. For **7** the retention time t_R = 21.6 min, while for **6** t_R = 23.2 min.

Procedures for Competition Experiments in 1,2-Dichloroethane. Experiments with $Yb(OTf)_3$. To a 20 mL round-bottom flask were added **1** (46.8 mg, 0.225 mmol), naphthalene (12.8 mg, 0.1 mmol) and 1,2-dichloroethane (10 mL), and the solution was mixed. $Yb(OTf)_3$ was added, and the reaction mixture was stirred for 15 min. The solution was purged with dry air for 5 min, and CCl_4 (48 μL, 0.495 mmol), 1-hexene (140 μL, 1.125 mmol), and triethylborane (56 μL, 0.056 mmol, 1 N in hexanes) were added sequentially. The flask was capped with a drying tube and stirred for between 30 min and 1 h. The mixture was diluted with ether (75 mL), washed with saturated ammonium chloride solution, dried over $MgSO_4$, and concentrated in vacuo. Conversion of **1** and product ratios were determined by GC analysis.

Experiments with $Sc(OTf)_3$. As in the protocol above, **1** (23.4 mg, 0.112 mmol), CCl_4 (192 μL, 1.98 mmol), 1-hexene (140 μL, 1.125 mmol), triethylborane (28 μL, 0.028 mmol), and 1,2-dichloroethane (10 mL) were used as starting materials. Conversion of **1** and product ratios were determined by GC analysis.

Acknowledgment. This research was supported by grants from the NIH (HL 17921) and the NSF (CHE-0107697).

Supporting Information Available: Experimental conditions and characterization of precursors and products. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0201676

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(18) Charges were evaluated using Mulliken population analyses, at the AM1/PM3 minimum geometry with a DFT single-point density, $\Delta C(C{-}Br) = C_C - C_{Br}$, thus positive values for $C^{\delta+} - Br^{\delta-}$ and negative values for $C^{\delta-} - Br^{\delta+}$.

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