Acyl-Transfer Mechanisms Involving Various Acyl Functional Groups: >X═Y with X = C, S, P and Y = O, S

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Abstract: Mechanisms of the gas-phase acyl group transfers, $Cl^- + R(X{=}Y)Cl$, involving various acyl functional groups, >X═Y with X = C, S, or P and Y = O or S, are investigated theoretically at the MP2/6-31+G* and B3LYP/6-31+G* levels (additionally with extended basis sets of B3LYP/6-311+G(3df,2p)), and the effects of solvent ($\epsilon = 78.5$) are calculated with the SCIPCM model at the isodensity level of 0.0004 au. The tetrahedral adducts formed in the carbonyl (RC═O) and thiocarbonyl (RC═S) group transfers are either transition states (double-well PES) or intermediates (single- or triple-well PES) depending on R, a stronger electron acceptor R favoring the intermediate. However, all of the sulfonyl (RSO_2) and phosphoryl ($(RO)_2P{=}O$) transfers proceed with trigonal bipyramid (TBP)-type transition states, in contrast to the stepwise mechanism through TBP-type intermediates for the sulfinyl (RS═O) (and sulfonyl transfers between F^-) transfers. The most important factor determining whether an adduct in an acyl-group-transfer reaction is the transition state or intermediate is the energy gap between the $\pi^*_{X=Y}$ and σ^*_{X-LG} orbitals. The possibility of reacting through an intermediate is greater for lower $\pi^*_{X=Y}$ and higher σ^*_{X-LG} levels. The backside σ-attack pathway is favored over the π-attack pathway only when a low-lying σ^*_{X-LG} orbital, preferably below the $\pi^*_{X=Y}$ level, is available. In general, the results are in good agreement with those of experiments. The solvent effect elevates the barrier height almost uniformly so that the relative orders of gas-phase activation barriers between different R groups are maintained in solution.

Introduction

The addition of nucleophiles (Nu) to the acyl group (RXY−) of acid derivatives is an important process in many synthetic routes in organic chemistry and biochemistry. Mechanisms of such reactions can be discussed in the context of the acyl group transfer between two nucleophiles as an acceptor and donor (LG), eq 1.[1]

$$\mathrm{Nu} + \mathrm{RXY{\cdot}LG} \rightleftharpoons [\mathrm{Nu{\cdot}RXY{\cdot}LG}] \rightleftharpoons \mathrm{Nu{\cdot}RXY} + \mathrm{LG} \quad (1)$$

The term "acyl" refers normally to the "carbonyl" group (RCO−; **I**), but it may be used as a general term to represent any group (RXY−) derived from acids (RXY−OH), e.g., thiocarbonyl (RCS−; **II**), sulfonyl (RSO_2−; **III**), sulfinyl (RSO−; **IV**), and neutral phosphoryl ($(RO)_2PO$−; **V**).[1,2]

The two most common heterolytic mechanisms involving nucleophilic acceptors, eq 1, are (i) *concerted*, in which the adduct, [Nu·RXY·LG] in eq 1, is a transition state (TS), and (ii) *stepwise*, in which the adduct is an intermediate with its formation or breakdown as the rate-determining step.[1,2] There are several factors that are in favor of the stepwise carbonyl-group-transfer mechanism with rate-limiting expulsion of the leaving group (LG) from a tetrahedral intermediate:[1−3] (i) The C═O π bond is weaker than the bond to the LG (C−LG). Therefore, the stronger the C−LG bond, the greater is the possibility of stable adduct formation. The C−F (BE = 116 kcal mol^{-1}) bond is much stronger than the C−Cl bond (BE = 79 kcal mol^{-1}),[3h] so carbonyl fluorides have a much greater possibility for a stepwise mechanism than carbonyl chlorides. (ii) The energy gap ($\Delta\epsilon = \epsilon(\sigma^*) - \epsilon(\pi^*)$) between the two antibonding orbitals, σ^*_{C-LG} and $\pi^*_{C=O}$ is wider, since the mixing of these two MOs upon initial molecular deformation leads to transformation of the σ^*_{C-LG} as a main component of the LUMO and results in a facile bond cleavage of the C−LG bond in the TS. (iii) The polarity (or dielectric constant) of the reaction medium is stronger, since the solvation of negative charge density on the oxygen helps to stabilize the tetrahedral intermediate.

Although the mechanism of acyl-transfer reactions involving the carbonyl group (**I**) has been extensively studied both in the gas phase[3] (experimentally[3a−d] as well as theoretically[3e−i]) and in solution,[4] theoretical studies on the acyl transfers of other groups (**II**−**V**) are relatively scarce. In this work, we investigated theoretically the gas-phase identity acyl-transfer reactions,

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[1] (a) Page, M. I.; Williams, A. *Organic and Bio-organic Mechanisms*; Longman: Harlow, 1997. (b) Williams, A. *Concerted Organic and Bio-organic Mechanisms*; CRC Press: Boca Raton, 2000.

[2] Williams, A. *Chem. Soc. Rev.* **1994**, *23*, 93.

[3] (a) Asubiojo, O. I.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 3715. (b) Wilbur, J. L.; Brauman, J. I. *J. Am. Chem. Soc.* **1994**, *116*, 9216. (c) Han, C. C.; Brauman, J. I. *J. Am. Chem. Soc.* **1990**, *112*, 7835. (d) Tanner, S. D.; Mackay, G. I.; Bohme, D. K. *Can. J. Chem.* **1981**, *59*, 1615. (e) Yamabe, S.; Minato, T. *J. Org. Chem.* **1983**, *48*, 2972. (f) Madura, J. D.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 2517. (g) Blake, J. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1987**, *109*, 3856. (h) Lee, I.; Lee, D.; Kim, C. K. *J. Phys. Chem. A* **1997**, *101*, 879. (i) Zhan, C.-G.; Landry, D. W.; Ornstein, R. L. *J. Am. Chem. Soc.* **2000**, *122*, 1522.

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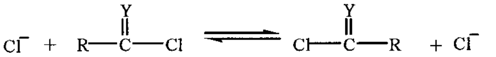
eq 1 with Nu = LG = Cl and R = MeO, Me, H, or CN, involving five types of acyl functional groups, **I**−**V**. We have also carried out calculations of solvent effects on the reactions using the SCIPCM model.[5] The purpose of this work is to explore the effects of the acyl functional groups (**I**−**V**) and solvent on the mechanism of the acyl-transfer reactions, eq 1.

Computational Details

All calculations were carried out using the Gaussian 94 and 98 software packages.[6] Geometries were optimized fully at the Hartree−Fock (RHF), MP2, and B3LYP[7] levels of theory using the 6-31+G* basis sets. Characterizations of the stationary points were carried out by harmonic vibrational analysis employing energy Hessians at the same three levels, RHF/6-31+G*, MP2/6-31+G*, and B3LYP/6-31+G*. For the selected transfer reactions, characterizations of the adducts were also carried out at a higher level of B3LYP/6-311+G(3df,2p). The energies (ΔE) were corrected for zero-point vibrational energies (ZPE) with application of appropriate scaling factors and thermal energies (ΔH) and application of entropies (ΔS) to obtain free energy changes (ΔG) at 298 K. For the density functional theory (DFT) energy calculations, single-point calculations were also performed with the extended basis sets at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G* level.[5d,8] Natural bond orbital (NBO) analyses[9] were applied to calculate the proximate $\sigma-\sigma^*$ (including n−σ^*, n−π^*, etc.) charge-transfer energies. The solvent effect was calculated using the isodensity polarizable continuum (IPCM) and self-consistent IPCM (SCIPCM) models at the isodensity level of 0.0004 au in water ($\epsilon = 78.5$).[5] In the former the cavity is defined as an isodensity surface of the molecule determined by the gas-phase MOs, but in the latter the isodensity surface is determined self-consistently in the presence of the polarizable medium. For comparison, calculations involving the isodensity level of 0.001 au and solvents with lower dielectric constants, $\epsilon = 2.0$ (cyclohexane), 8.9 (dichloromethane), and 36.6 (acetonitrile), were also performed.

Results and Discussion

(A) Identity Carbonyl (I; RC=O) and Thiocarbonyl (II; RC=S) Group Transfers. Selected geometrical parameters involved in the identity transfers of carbonyl (**I**) and thiocarbonyl (**II**) groups, eq 2, are summarized in Table S1 (Supporting Information). The reactants have planar structures, whereas the transition states (TS, R = MeO, Me, and H for **I**, and MeO and Me for **II**) and intermediates (Int. R = CN for **I**, and H and CN for **II**; vide infra) have tetrahedral structures.



$$\mathrm{Cl^- + R{-}\overset{\overset{Y}{\|}}{C}{-}Cl \rightleftharpoons Cl{-}\overset{\overset{Y}{\|}}{C}{-}R + Cl^-} \qquad (2)$$

where I : Y = O and II : Y = S with R = MeO, Me, H or CN

In both **I** and **II**, the B3LYP bond lengths of C−Cl (d_{C-Cl}) are longer (by ca. 0.02−0.03 Å), but those of C=Y ($d_{C=O}$ or $d_{C=S}$) are shorter (by ca. 0.01−0.02 Å) than those calculated by the MP2 method. Additionally, the B3LYP angles ∠Cl−C−Cl in the TS and intermediate are smaller by ca. 1−2° than those calculated by the MP2 method. Adduct (TS or Int.) formation leads to stretching of both d_{C-Cl} and $d_{C=Y}$, but the stretching of d_{C-Cl} is greater in **I** than in **II**, whereas the stretching of $d_{C=Y}$ is greater in **II** than in **I**. The greater stretching of C=S than C=O in the adduct suggests a greater polarizability of the C=S bond (to C^+-S^-) than C=O (to C^+-O^-) as is well known.[10] Since in the adduct the greater polarizability of the C=S bond leads to a greater electron deficiency on the carbon in **II**, the angle ∠Cl−C−Cl seems to open somewhat wider in **II** than in **I**.

Loose reactant complexes (RCs) are formed electrostatically between Cl^- and the reactants. The structures and energies are given in Table S2 (Supporting Information). Since the reactions are identity exchanges, the thermodynamic barriers are zero so that the barrier heights from the reactant complexes are intrinsic barriers, $\Delta E^{\ddagger}_{o}$. The intrinsic barriers, $\Delta E^{\ddagger}_{o}$, for the selected reactions are given in the tables for energetics (Tables 1, 2, 4, 5, and 6).

Energetics for the carbonyl and thiocarbonyl group transfers are summarized in Tables 1 and 2, respectively. As reported earlier, the identity carbonyl (**I**) transfer proceeds through a single- or triple-well potential energy surface (PES),[3h] which corresponds to a stepwise reaction proceeding through an intermediate in solution, but with a strong electron acceptor group, R = CN. The B3LYP results show fundamentally the same relative order and the nature of the adducts, i.e., TS or intermediate, given by the MP2 method. We note that the RHF results predict double-well PESs, which corresponds to a reaction through a tetrahedral TS in solution, for all acyl groups including R = CN. Higher level DFT calculations with an extended basis set, B3LYP/6-311+G(3df,2p), show lowering of adduct levels, by ca. 0.5 kcal mol^{-1}, and in solution (SCIPCM results) all of the acyl groups are predicted to proceed via double-well PESs (including R = CN).

The gas-phase carbonyl transfer through a stable intermediate (single-well PES) predicted for R = CN, in contrast to the concerted (double-well PES) reaction pathway for other weaker electron-withdrawing groups, R = MeO, CH_3, and H, stems from a weakening of the $\pi_{C=O}$ bond by lowering of the $\pi^*_{C=O}$

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[4] (a) Gresser, M. J.; Jencks, W. P. *J. Am. Chem. Soc*. **1977**, *99*, 6963, 6970. (b) Hupe, D. J.; Jencks, W. P. *J. Am. Chem. Soc*. **1977**, *99*, 453. (c) Castro, E. A.; Gil, F. J. *J. Am. Chem. Soc*. **1977**, *99*, 7611. (d) Castro, E. A.; Freundenberg, M. *J. Org. Chem*. **1980**, *45*, 906. (e) Castro, E. A.; Santander, C. L. *J. Org. Chem*. **1985**, *50*, 3595. (f) Castro, E. A.; Ruiz, M. G.; Salinas, S.; Santos, J. G. *J. Org. Chem*. **1999**, *64*, 4817. (g) Ba-Saif, S.; Luthra, A. K.; Williams, A. *J. Am. Chem. Soc*. **1989**, *111*, 2647. (h) Hengge, A. *J. Am. Chem. Soc*. **1992**, *114*, 6575. (i) Koh, H. J.; Kim, S. I.; Lee, B. C.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1353. (j) Koh, H. J.; Shim, C. H.; Lee, H. W.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1329. (k) Koh, H. J.; Han, K. L.; Lee, H. W.; Lee, I. *J. Org. Chem*. **1998**, *63*, 9834. (l) Menger, F. M.; Smith, J. H. *J. Am. Chem. Soc*. **1972**, *94*, 3824.

[5] (a) Wiberg, K. B.; Rablen, P. R.; Rush, D. J.; Keith, T. A. *J. Am. Chem. Soc*. **1995**, *117*, 4261. (b) Foresman, J.; Keith, T. A.; Wiberg, K B.; Snoonian, J.; Frisch, M. *J. Phys. Chem*. **1996**, *100*, 16098. (c) Rablen, P. R.; Pearlman, S. A.; Miller, D. A. *J. Am. Chem. Soc*. **1999**, *121*, 227. (d) Foresman, J. B.; Feisch, Æ. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, 1993.

[6] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S. Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98, Revision A.6*; Gaussian, Inc.: Pittsburgh, PA, 1998.

[7] (a) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

[8] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

[9] (a) Reed, R. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev*. **1988**, *88*, 899. (b) Glendening, E. D.; Weinhold, F. *J. Comput. Chem*. **1998**, *19*, 610. (c) Glendening, E. D.; Badenhoop, J. K.; Weinhold, F. *J. Comput. Chem*. **1998**, *19*, 628.

[10] (a) Hadad, C. M.; Rablen, P. R.; Wiberg, K. B. *J. Org. Chem*. **1998**, *63*, 8668. (b) Abboud, J.-L. M.; Mo, O.; De Paz, J. L. G.; Yanez, M.; Esseffar, M.; Bouab, W.; El-Mouhtadi, M.; Mokhlrisse, R.; Ballesteros, E.; Herreros, M.; Homan, H.; Lopez-Mardomingo, C.; Notario, R. *J. Am. Chem. Soc*. **1993**, *115*, 12468.

Table 1. Energetics for Carbonyl-Transfer Reactions, Eq 2, Calculated by Various Methods with the 6-31+G* Basis Set[a] (in kcal mol^{-1})

method	R	$\Delta E^{b,c}$		ΔH^b	$-T\Delta S^b$	ΔG^b
RHF	MeO	20.94	(298i cm^{-1})^d	19.82	9.52	29.3
	Me	4.09	(99i cm^{-1})^d	4.17	5.70	9.9
	H	6.01	(370i cm^{-1})^d	5.30	7.77	13.1
	CN	−3.74	(165i cm^{-1})^d	−4.49	9.96	5.5
MP2	MeO	1.66	(124i cm^{-1})^d	0.92	8.82	9.7
	Me	−5.19	(97i cm^{-1})^d [−6.16]^i	−5.96	8.73	2.8
	H	−7.41	(93i cm^{-1})^d [−8.27]^i	−8.22	8.07	−0.2
	CN	−21.80	(Int.)^e [−22.46]^i	−22.06	7.75	−14.3^k
B3LYP	MeO	3.63	(142i cm^{-1})^d	3.04	8.32	11.4
	Me	−4.67	(116i cm^{-1})^d	−5.37	8.51	3.1
	H	−9.76	(99i cm^{-1})^d (8.04)^j	−10.54	7.95	−2.6
	CN	−19.96	(Int.)^e	−20.15	7.43	−12.7^k
B3LYP (ext)^f	MeO	3.11	(TS)	2.52	8.32	10.8
	Me	−5.12	(TS)	−5.82	8.51	2.7
	H	−10.18	(TS)	−10.96	7.95	−3.0
	CN	−20.69	(Int.)	−20.88	7.43	−13.5
SCIPCM^g	MeO^h	19.35	−	18.71	8.49	27.2
	Me	9.31	(190i cm^{-1})^d	8.68	8.31	17.0
	H	4.54	(179i cm^{-1})^d	3.78	7.95	11.7
	CN	−1.23	(105i cm^{-1})^d	−1.88	8.54	6.7

[a] Geometries of reactant and tetrahedral adduct were constrained to C_s symmetry. The reactant energies (E) for R = MeO, Me, H, and CN are −1147.06724 (−1148.89827), −1072.03276 (−1073.68308), −1032.87889 (−1034.38126), and −1124.88003 (−1126.60833) au, respectively, at the MP2 (B3LYP) level. Zero-point vibrational energies were scaled by 0.9670, 0.9806, and 0.9806 respectively for the MP2, B3LYP, and SCIPCM levels; scaling factors are taken from Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502. RHF zero-point vibrational energies were not scaled. [b] Differences between adducts and separated reactants; ΔS at 298.15 K. [c] Corrected for zero-point vibrational energy. [d] Transition state, confirmed by only one negative eigenvalue in the Hessian matrix. [e] Intermediate, confirmed by all positive eigenvalues in the Hessian matrix. [f] Calculated with extended basis sets, B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G*. [g] At the B3LYP/6-31+G* level; dielectric constant ϵ = 78.5, isodensity of 0.0004 au. This ΔE includes solvation energies, ΔG_s. [h] Adducts failed to converge. The electronic energy is calculated by using gas-phase geometry, and thermal energy data are taken from the gas-phase results. We found that the thermal energies in the gas phase and in the solution phase differ within 0.3 kcal mol^{-1} in other cases (R = Me, H, CN). [i] The ΔE values at the MP4/6-31+G*//MP2/6-31+G* level.[3h] [j] The intrinsic barrier, $\Delta E^{\ddagger}_{o} = \Delta E^{\ddagger} - \Delta E(\mathrm{RC})$. [k] Single-well PES.

Table 2. Energetics for Thiocarbonyl-Transfer Reactions, Eq 2, Calculated by Various Methods with the 6-31+G* Basis Set[a] (in kcal mol^{-1})

method	R	$\Delta E^{b,c}$		ΔH^b	$-T\Delta S^b$	ΔG^b
RHF	MeO	13.60	(110i cm^{-1})^d	12.67	9.44	22.1
	Me	7.14	(287i cm^{-1})^d	6.29	9.03	15.3
	H	−1.38	(Int.)^e	−2.11	8.28	6.2
	CN	−10.08	(Int.)^e	−10.68	8.72	−2.0
MP2	MeO	2.33	(121i cm^{-1})^d	1.50	9.24	10.7
	Me	−5.09	(Int.)^e	−5.72	8.75	3.0 (4.3)^k
	H	−6.97	(Int.)^e	−7.57	8.02	0.5 (1.7)^k
	CN	−18.22	(Int.)^e	−18.57	8.21	−10.4^l
B3LYP	MeO	4.98	(135i cm^{-1})^d	4.41	8.50	12.9
	Me	−3.60	(33i cm^{-1})^d	−4.36	8.86	4.5
	H	−9.02	(Int.)^e (4.64)^j	−9.32	7.14	−2.2 (−1.6)^k
	CN	−16.88	(Int.)^e	−17.03	7.60	−9.4^l
B3LYP (ext)^f	MeO	4.55	(TS)	3.98	8.50	12.5
	Me	−3.85	(TS)	−4.61	8.86	4.3
	H	−9.32	(Int.)	−9.62	7.14	−2.5
	CN	−17.69	(Int.)	−17.84	7.60	−10.2
SCIPCM^g	MeO^h	21.12	−	19.77	10.59	30.4
	Me	13.44	(105i cm^{-1})^d	12.76	8.73	21.5
	H	7.56	(Int.)^e	7.27	7.08	14.4 (14.8)^{k,m}
	CN	3.73	(Int.)^e	3.60	7.56	11.2

[a] Geometries of reactant and tetrahedral adduct were constrained to C_s symmetry. The reactant energies (E) for R = MeO, Me, H, and CN are −1469.63553 (−1471.84032), −1394.60274 (−1396.62539), −1355.45208 (−1357.32827), and −1447.46105 (−1449.56150) au, respectively, at the MP2 (B3LYP) level. Zero-point vibrational energies were scaled by 0.9670, 0.9806, and 0.9806 respectively for MP2, B3LYP, and SCIPCM levels; scaling factors are taken from Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502. RHF zero-point vibrational energies were not scaled. [b−j] Same as those in Table 1. [k] The TS level. [l] Single-well PES. [m] $\Delta G^{\ddagger}_{o} = \Delta G^{\ddagger}(\mathrm{gas}) + \delta\Delta G^{\ddagger}_{s}$, where $\delta\Delta G^{\ddagger}_{s} = \Delta G^{\ddagger}_{s} - \Delta G_{s}(\mathrm{React.})$; $\Delta G^{\ddagger}_{s}$ and $\Delta G_{s}(\mathrm{React.})$ are the solvation energies for transition state and reactants respectively, which are calculated at the SCIPCM/B3LYP/6-31+G*//B3LYP/6-31+G* level.

Table 3. Canonical MO Levels of $\pi^*_{\mathrm{X=Y}}$ and $\sigma^*_{\mathrm{C-Cl}}$ for the Reactants, Calculated at RHF/6-31+G*//B3LYP/6-31+G* (in au)

acyl type	R	$\epsilon(\pi^*_{\mathrm{X=Y}})$	$\epsilon(\sigma^*_{\mathrm{C-Cl}})$	$\Delta\epsilon(\sigma^*_{\mathrm{C-Cl}}-\pi^*_{\mathrm{X=Y}})$
carbonyl−Cl	MeO	+0.143	+0.238	0.095
	Me	+0.105	+0.221	0.116
	H	+0.079	+0.235	0.156
	CN	+0.021	+0.219	0.198
thiocarbonyl−Cl	MeO	+0.061	+0.219	0.158
	Me	+0.034	+0.208	0.174
	H	+0.023	+0.209	0.186
	CN	−0.030	+0.188	0.218
sulfonyl−F	Me	+0.053	+0.163	0.110
	H	+0.049	+0.156	0.107
	CN	+0.051	+0.136	0.085
sulfonyl−Cl	Me	+0.037	+0.088	0.051
	H	+0.027	+0.096	0.069
	CN	+0.005	+0.087	0.082
sulfinyl−Cl	Me	+0.029	+0.099	0.070
	H	+0.014	+0.095	0.081
	CN	−0.013	+0.091	0.104
phosphoryl−Cl	Me	+0.069	+0.190	0.121
	H	+0.049	+0.175	0.126

sufficiently to facilitate formation of the tetrahedral intermediate ($\pi^*_{\mathrm{C=O}}$ for R = CN is lower by ca. 0.06 au than that for R = H in Table 3).

We also note in Table 1 that the MP2 $\Delta E^{\ddagger}$ values for R = Me, H, and CN are somewhat closer to the higher level MP4 results than the corresponding B3LYP values, although the relative orders are not changed. The inclusion of zero-point and thermal corrections to the energy ($\Delta H^{\ddagger}$), as well as the entropy ($\Delta G^{\ddagger}$), does not change the relative order given by potential energies ($\Delta E^{\ddagger}$) in both Tables 1 and 2.

The MP2 results for the thiocarbonyl group transfers in Table 2 predict a stepwise mechanism through an intermediate (triple-well PESs for R = Me and H, and single-well PES for R = CN), but of all the other methods reactions through an intermediate are predicted only for the latter two, R = H and CN. These results nevertheless indicate that thiocarbonyl group transfers have a greater tendency to react through anionic adducts as intermediates rather than TSs compared to carbonyl transfers.[11] This trend is consistent with the weaker π bond strength of C=S (the π bond energy is lower by ca. 30 kcal mol^{-1} than that of C=O,[12] and π^* level is low at 0.023 au for R = H, Table 3) than C=O (the π^* level is high at 0.079 au[13] for R = H, Table 3), which leads to a more facile bond cleavage of C=S to form a tetrahedral intermediate, T$^-$(S$^-$), and to a greater stability for T$^-$(S$^-$) than the corresponding adduct, T$^-$(O$^-$), since reversion to C=S double bond gains less energy

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(11) Castro, E. A. *Chem. Rev.* **1999**, *99*, 3505.

(12) Cottrell, T. L. *The Strengths of Chemical Bonds*, 2nd ed.; Butterworth: London, 1958; p 275.

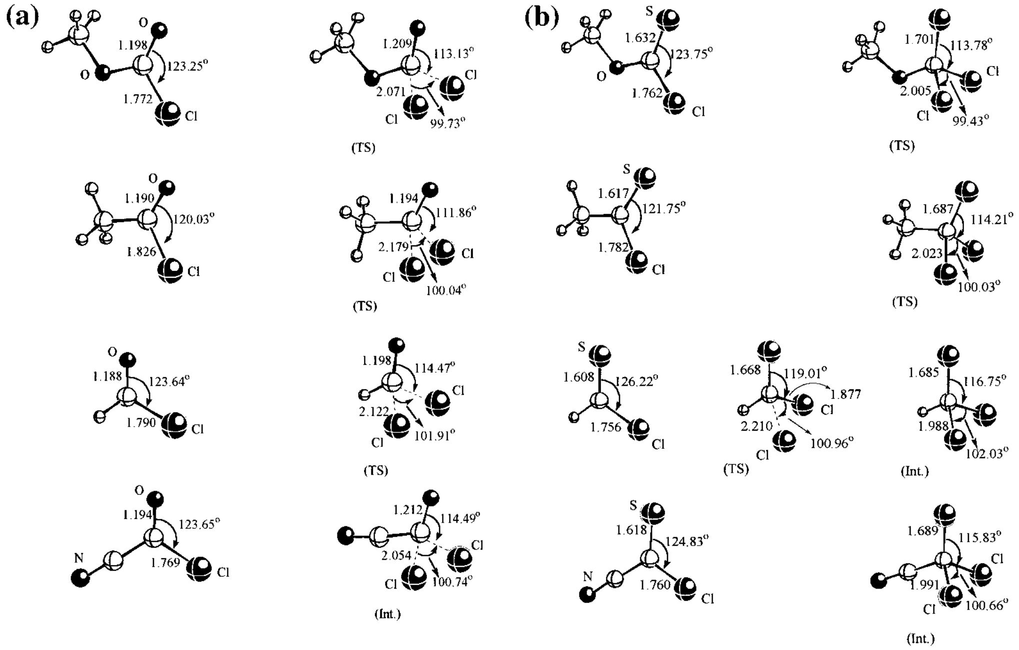
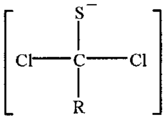
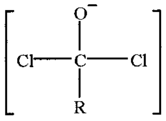


Figure 1. (a) Structures of reactants and adducts for carbonyl-transfer reactions (bond lengths in angstroms, and angles in degrees), calculated at the B3LYP/6-31+G* level. (b) Structures of reactants and adducts for thiocarbonyl-transfer reactions (bond lengths in angstroms, and angles in degrees), calculated at the B3LYP/6-31+G* level.

than that to C=O.[11,14,15] We note in Table 3 that the $\pi^*_{\mathrm{C=S}}$ levels are much lower than the $\pi^*_{\mathrm{C=O}}$ levels, which leads to a greater tendency for the thiocarbonyl transfer to proceed via an intermediate (single- or triple-well PES). The reactants' and adducts' structures at the B3LYP/6-31+G* level are presented in Figure 1.



$\mathrm{T^-(S^-)}$



$\mathrm{T^-(O^-)}$

The percentage changes of bond order ($\%\Delta n^{\ddagger}$)[16] upon adduct formation (TS or intermediate) are shown for the C−Cl and C=Y bonds in Table S1. In the carbonyl transfers, ca. 40% stretching of the C−Cl bond and 1−6% stretching of C=O take place. In contrast, however, in the thiocarbonyl transfers the stretching of C−Cl is only 22−33%, with a much larger stretching of C=S (ca. 21−28%) than the corresponding changes in the carbonyl transfer. On the whole, thus, deformation energies[17] (ΔE_{def} in Table S3, Supporting Information) are similar in the two transfer reactions. On the other hand, the proximate $\sigma-\sigma^*$ (including $n-\pi^*$, $n-\sigma^*$, etc.) charge-transfer stabilization[9,18,19b] is greater in the carbonyl than in the thiocarbonyl transfers, whereas the electrostatic interactions are more destabilizing in the thiocarbonyl rather than carbonyl transfers. This suggests that in the carbonyl transfers charge-transfer delocalization is the predominant TS stabilizing factor, but in the thiocarbonyl transfer the electrostatic interaction is the major destabilizing factor, which is reasonable since the thiocarbonyl group is polarized ($\mathrm{C^+-S^-}$) strongly in the TS (or intermediate) as the $\%\Delta n^{\ddagger}$ values indicated (Table S1), and so repulsive interactions between the three negative charge centers, the two $\mathrm{Cl^-}$ and $\mathrm{S^-}$, are large. The deformation energies (ΔE_{def}), electrostatic (ΔE_{es}) energies, and proximate $\sigma-\sigma^*$ charge-transfer interaction energies are summarized in Table S3.

In all cases, irrespective of whether the adduct is a TS (concerted) or an intermediate (stepwise), the carbonyl transfer has a somewhat lower activation barrier and a more stable intermediate than the corresponding thiocarbonyl transfers in the gas phase as well as in solution. In this respect, it is interesting to note that the aminolysis of carbonyl esters exhibited greater reactivity than thiocarbonyl esters in the concerted processes, whereas it reverses to the greater reactivity with thiocarbonyl esters when the mechanism changes to stepwise with rate-limiting expulsion of the leaving group from a tetrahedral zwitterionic intermediate, $\mathrm{T^{\pm}}$, in aqueous as well as in acetonitrile solution.[15c,d,20] This latter reversion is most probably due to the easier cleavage of C=S than of C=O π bond and the greater stability of $\mathrm{T^-(S^-)}$ than of $\mathrm{T^-(O^-)}$.[14,15]

Reported gas-phase experimental results are rather limited to the carbonyl-transfer reactions. Brauman and co-workers[3a−c] reported their ion cyclotron resonance results on the carbonyl transfers including halide ion reactions with carbonyl halides

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[13] Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R. L.; Bernardi, F. *Structural Theory of Organic Chemistry*; Springer-Verlag: Berlin, 1977; Part I.

[14] Hill, S. V.; Thea, S.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 437.

[15] (a) Castro, E. A.; Ibanez, F.; Santos, J. G.; Ureta, C. *J. Chem. Soc., Perkin 2* **1991**, 1919. (b) Castro, E. A.; Araneda, C. A.; Santos, J. G. *J. Org. Chem.* **1997**, *62*, 126. (c) Oh, H. K.; Kim, S. K.; Cho, I. H.; Lee, H. W.; Lee, I. Submitted.

[16] (a) Houk, K. N.; Gustabson, S. M.; Black, K. A. *J. Am. Chem. Soc.* **1992**, *114*, 9565. (b) Lee, I.; Kim, C. K.; Lee, B. S. *J. Comput. Chem.* **1995**, *16*, 1045. (c) Lee, J. K.; Kim, C. K.; Lee, I. *J. Phys. Chem. A* **1997**, *101*, 2893.

[17] (a) Mitchell, D. J.; Schlegel, H. B.; Shaik, S. S.; Wolfe, S. *Can. J. Chem.* **1985**, *63*, 1642. (b) Shaik, S.; Schlegel, H. B.; Wolfe, S. *Theoretical Aspects of Physical Organic Chemistry. The S_N2 Mechanism*; Wiley: New York, 1992.

[18] Ref 13, Parts III and IV.

[19] (a) Glukhovtzev, M. N.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1994**, *116*, 5961. (b) Kim, C. K.; Hyun, K. H.; Kim, C. K.; Lee, I. *J. Am. Chem. Soc.* **2000**, *122*, 2294.

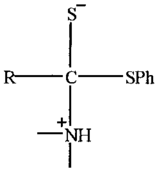
[20] (a) Castro, E. A.; Pizarro, M. I.; Santos, J. G. *J. Org. Chem.* **1996**, *5982*, 61. (b) Oh, H. K.; Kim, S. K.; Lee, I. *Bull. Korean Chem. Soc.* **1999**, *20*, 1017.

in the gas phase. Their kinetic results exhibited double-well PESs with the tetrahedral transition state and the two ion−dipole complexes at the energy minima. In contrast, however, Tanner et al.[3d] have shown that in the gas-phase reactions of strong nucleophiles, H^-, OH^-, and CH_3O^-, with $H_2C{=}O$, stable tetrahedral adducts are produced. Subsequent theoretical works have led to clarification of the two conflicting experimental results:[3e−h] the stronger the attacking nucleophile and the weaker the leaving group (nucleofuge), the more likely is the tetrahedral adduct involved in a carbonyl-transfer reaction to be a stable intermediate.

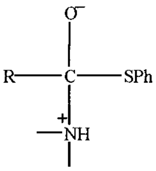
Experimentally in solution, the Brønsted-type plots, eq 3, for reactions of amine nucleophiles with carbonyl (**I**) and thiocarbonyl (**II**) esters have often been found to show a break from

$$\log k_N = \beta_{nuc}\, pK_a + \text{const} \tag{3}$$

a large ($\beta_{nuc} \geq 0.8$) to a small ($\beta_{nuc} \leq 0.3$) dependence of the rate (k_N) on the basicity (pK_a) of the attacking amine nucleophile, which has been interpreted to indicate a mechanistic change from a breakdown to formation of the tetrahedral intermediate.[1] Such a biphasic rate dependence on the basicity of the nucleophile has been obtained in the reactions of alicyclic amines with *O*-ethyl *S*-(2,4-dinitrophenyl)dithiocarbonate ($EtO{-}C({=}S){-}SC_6H_3(NO_2)_2$),[15b] whereas the same plot is linear with $\beta_{nuc} = 0.56$ in the reactions of the same amines with *O*-ethyl *S*-(2,4-dinitrophenyl)thiocarbonate ($EtO{-}C({=}O){-}SC_6H_3(NO_2)_2$).[21] The change of thiocarbonyl to carbonyl destabilizes the tetrahedral intermediate so that a stepwise mechanism for the thiocarbonyl changes to a concerted mechanism for the carbonyl compound. Another important mechanistic change due to the tetrahedral intermediate being more stabilized with thiocarbonyl than with carbonyl was observed: slower rates of expulsion of both PhS^- and a given amine from intermediate $T^{\pm}(S^-)$ than from $T^{\pm}(O^-)$ resulted in a complex kinetic expression, in which the proton-transfer step is explicitly included, for the reactions through $T^{\pm}(S^-)$[15a,22] in contrast to a well-known simple form,[4] $k_N = k_a/k_{-a}k_b = K_ak_b$, where k_a, k_{-a}, and k_b are the rates of amine addition, amine, and PhS^- expulsion from $T^{\pm}$, respectively, for the reactions involving $T^{\pm}(O^-)$. The complex expression has been shown to arise because of a competitive proton transfer with the expulsion of PhS^- from $T^{\pm}(S^-)$ in aqueous solution.[15a,22] This competitive proton transfer, however, disappears in aprotic solvents, e.g., acetonitrile,[23] due to slow proton transfer, and the rate constant expression simplifies again to $k_N = K_ak_b$.



$T^{\pm}(S^-)$



$T^{\pm}(O^-)$

In addition to the π bond strength of C═S being weaker than that of C═O, the C═S bond is much more polarizable.[10b,11] According to the MP2 results, the NBO charge changes, Δq (Tables S4, Supporting Information), on going from the reactant to the adduct are $\Delta q_{(C)} = -0.04$ to -0.10 and $\Delta q_{(O)} = -0.11$ to -0.18 for C═O, whereas they are $\Delta q_{(C)} = -0.02$ to -0.04 and $\Delta q_{(S)} = -0.41$ to -0.55 for C═S. The NBO charge changes determined by B3LYP are also similar.

A major factor that determines whether the acyl transfers proceed through a stable tetrahedral adduct (with a single- or triple-well PES) or through a TS (with a double-well PES) involving an $sp^2 \rightarrow sp^3$ change of carbon is the MO level gap between σ^*_{C-Cl} and $\pi^*_{X=Y}$, $\Delta\epsilon = \epsilon(\sigma^*) - \epsilon(\pi^*)$.[3e,h,24] If the two MOs are separated by a large energy gap, the orbital mixing between the π^* and σ^* orbitals upon initial molecular deformation is small, and the approaching nucleophile forms a stable adduct through π approach. In contrast, when the energy gap is small enough to induce sufficient mixing of the two, π^* and σ^*, MOs, the σ^*_{C-Cl} MO becomes a main component of the LUMO so that charge transfer from the nucleophile leads to the weakening of the C−Cl bond and the reaction proceeds through a TS in a concerted process. This means that *the possibility of a transfer reaction through a single- or triple-well PES (by a stepwise mechanism) is greater for a lower* $\pi^*_{X=Y}$ *level and a higher* σ^*_{C-Cl} *level.* The π^* and σ^* levels are summarized in Table 3. We clearly see that the $\pi^*_{C=S}$ levels are much lower (by more than 0.05 au) but the σ^*_{C-Cl} levels are slightly lower (by 0.01−0.03 au), so that the level gaps, $\Delta\epsilon = \epsilon(\sigma^*) - \epsilon(\pi^*)$, are greater by more than 0.02−0.06 au for the thiocarbonyl transfers than for the corresponding carbonyl transfers, which are consistent with the greater tendency of the intermediate formation for the thiocarbonyl transfers.

Reference to Tables 1 and 2 reveals that a stronger electron acceptor R is more conducive to the stable adduct formation due to the increase in the $\pi^*-\sigma^*$ level gaps by depression of the $\pi^*_{X=Y}$ levels and resulting stabilization of the adduct, and the solvent (water) tends to raise the energy levels of adducts due to charge dispersion in the TS together with a decrease in dipole moment upon adduct formation.

The MP2 as well as B3LYP solvation energies were calculated by IPCM and SCIPCM methods with isodensity levels at 0.001 and 0.0004 au.[5] The results (Tables S6−S10, Supporting Information) show that, in general, solvation energies calculated at the two levels of theory, MP2 and B3LYP, do not differ significantly, with differences of less than 1 kcal mol^{-1} in most cases. Solvation stabilization is always greater (ΔG_s is more negative) with the reactants than with the adducts, so the differences $\delta\Delta G_s$ ($=\Delta G_s(\text{add.}) - \Delta G_s(\text{react.})$) are positive, and hence activation barriers for adduct formation are elevated due to solvent. The positive $\delta\Delta G_s$ values are seen to increase with the dielectric constant of the solvent, indicating a greater activation barrier in a more polar solvent.

The solvation stabilizations, $\Delta G^{\circ}_s < 0$, of the reactants and adducts are somewhat greater for the carbonyl than for the thiocarbonyl transfers. However, the solvation energy differences, $\delta\Delta G_s = \Delta G_s(\text{add.}) - \Delta G_s(\text{react.}) > 0$, are greater for the thiocarbonyl than for the carbonyl by ca. 1−4 kcal mol^{-1} since the differences in ΔG_s(add.) between the carbonyl and thiocarbonyl are greater than those in ΔG_s(react.). On the other hand, the use of isodensity level at 0.001 au leads to larger solvation energies (a greater negative ΔG°_s) compared to those at 0.0004 au level by ca. −8 kcal mol^{-1} for ΔG_s(react.) and by ca. −3 to −5 kcal mol^{-1} for ΔG_s(add.), and as a result the $\delta\Delta G_s$ (>0) values are smaller by ca. 3−4 kcal mol^{-1} when 0.001 au is used. At the same isodensity level of 0.0004 au, the self-

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[21] Castro, E. A.; Ibanez, F.; Salas, M.; Santos, J. G. *J. Org. Chem.* **1991**, *56*, 4819.

[22] (a) Castro, E. A.; Ibanez, F.; Santos, J. G.; Ureta, C. *J. Org. Chem.* **1992**, *57*, 7024. (b) Cabrera, M.; Castro, E. A.; Salas, M.; Santos, J. G.; Sepulveda, P. *J. Org. Chem.* **1991**, *56*, 5324.

[23] (a) Oh, H. K.; Woo, S. Y.; Shin, C. H.; Park, Y. S.; Lee, I. *J. Org. Chem.* **1997**, *62*, 5780. (b) Oh, H. K.; Lee, J. Y.; Yun, J. H.; Park, Y. S.; Lee, I. *Int. J. Chem. Kinet.* **1998**, *30*, 419.

[24] Kim, C. K.; Li, H. G.; Sohn, C. K.; Chun, Y. I.; Lee, I. *J. Phys. Chem. A* **2000**, *104*, 4069.

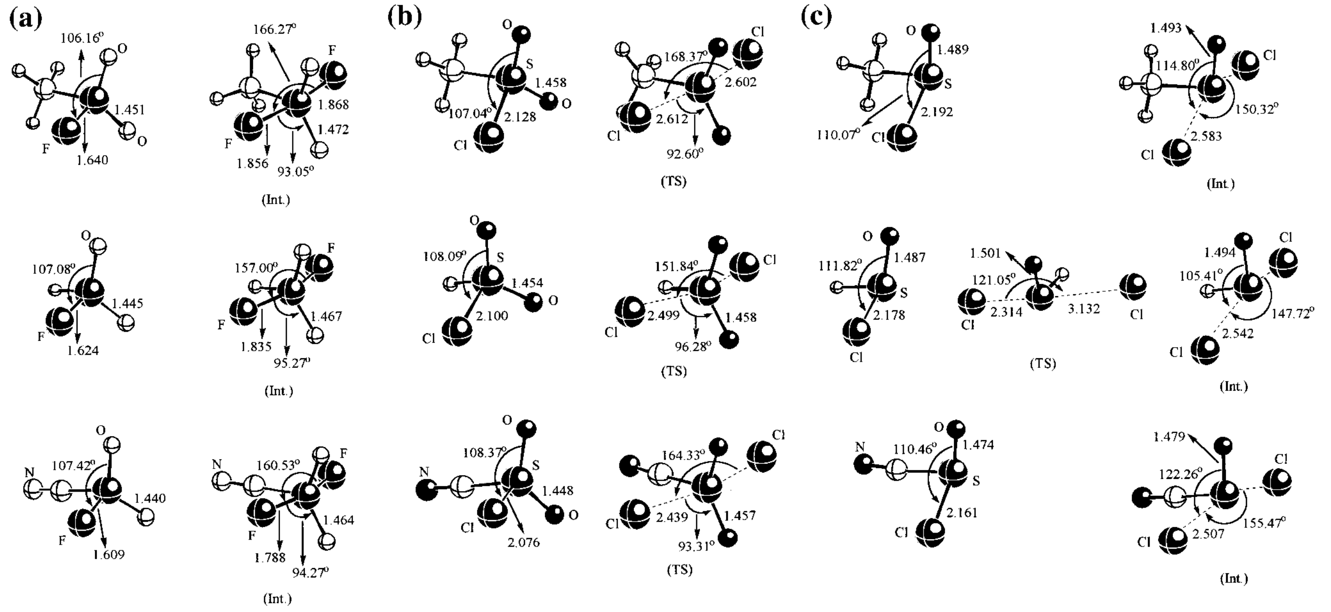


Figure 2. (a) Structures of reactants and adducts for sulfonyl-transfer reactions with Nu = LG = F^-, calculated at the B3LYP/6-31+G* level (bond lengths in angstroms, and angles in degrees). (b) Structures of reactants and adducts for sulfonyl-transfer reactions with Nu = LG = Cl^-, calculated at the B3LYP/6-31+G* level (bond lengths in angstroms, and angles in degrees). (c) Structures of reactants and adducts for sulfinyl-transfer reactions with Nu = LG = Cl^-, calculated at the B3LYP/6-31+G* level (bond lengths in angstroms, and angles in degrees).

consistent calculations (SCIPCM) give lower (smaller negative ΔG_s) solvation energies than IPCM model, by ca. 5 kcal mol^{-1} for the reactants and by ca. 7−8 kcal mol^{-1} for the adducts, leading to greater $\delta\Delta G_s$ (>0) values by ca. 1−3 kcal mol^{-1}. Overall, the IPCM model leads to larger solvation stabilization energies (larger negative ΔG_s) relative to the SCIPCM model, and the higher isodensity level of 0.001 au leads to greater solvation energies relative to those at the 0.0004 au level. In contrast, however, the solvation energy differences, $\delta\Delta G_s = \Delta G_s(\text{add.}) - \Delta G_s(\text{react.}) > 0$, are smaller with IPCM (compared to SCIPCM), and at the higher isodensity level, 0.001 au (compared to the value at 0.0004 au).

(B) Identity Sulfonyl (III; RSO$_2$−) and Sulfinyl (IV; RSO−) Group Transfers.


(4)

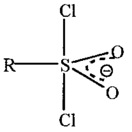
$$Cl^- + R{-}S(=O)_2{-}Cl \rightleftharpoons Cl{-}S(=O)_2{-}R + Cl^- \quad (4)$$


(5)

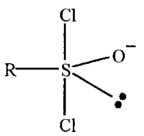
$$Cl^- + R{-}\ddot{S}(=O){-}Cl \rightleftharpoons Cl{-}\ddot{S}(=O){-}R + Cl^- \quad (5)$$

with R = Me, H or CN.

In both cases, the reactants, RSO$_2$−Cl and R$\ddot{S}$O−Cl, have tetrahedral structures, whereas the adducts have distorted trigonal-bipyramidal pentacoordinate (TBP-5C) structures, with the two most electronegative groups (Cl), which are the attacking nucleophile and the leaving group, occupying apical (or axial) positions.

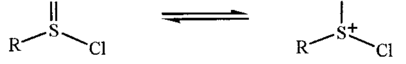


TBP(SO$_2$)



TBP(SO)

The two apical Cl and central S atoms in the adducts are not collinear, i.e., ∠Cl−S−Cl ≠ 180°, but ∠Cl−S−Cl ranges from ca. 152° to 168° in TBP(SO$_2$) and from ca. 148° to 156° in TBP(SO) due to repulsive effects between the two apical Cl atoms and the presence of two negatively charged oxygen atoms in the former and an oxygen and lone pair in the latter. The smaller angle subtended by the two Cl atoms in the latter (TBP-(SO)) should be indicative of the stronger repulsive effect of a lone pair in TBP(SO) than a polarized $S^+{-}O^-$ bond in TBP-(SO$_2$), as the valence-shell electron-pair repulsion (VSEPR) theory predicts.[25] The representative reactant and adduct structures are shown in Figure 2. Other selected geometrical parameters are collected in Table S5 (Supporting Information). We note that the S−O bond in sulfonyl is shorter by ca. 0.03 Å than that in the sulfinyl system, 1.487 Å for R = H, which is in reasonable agreement with 1.480 Å at the B3LYP/6-31+G-(d,p),S(3df) level, and 1.510 Å at the QCISD/6-31+G(d,p) level for the S−O bond in sulfine ($H_2CS{=}O$).[26b] The stretching of the S═O bond upon adduct (intermediate) formation in the RSO$_2$F system is substantial (ca. 0.02 Å for all R), but in the RSO$_2$Cl system it is very small (ca. 0.004 Å for R = H), since the adduct in this case is a TS (vide infra). The stretching of the S═O bond in the sulfinyl transfer (**IV**) is slightly greater than this (ca. 0.007 Å for R = H), despite the fact that the adduct is an intermediate (vide infra). This is because the sulfinyl group is partially polarized to a dipolar form in the reactant, so the additional stretching upon adduct formation should be small.[26b] This polarization effect is, however, smaller in the sulfonyl system. The NBO charges (Table S11, Supporting Information) show that the sulfur atom becomes more negative and oxygens



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[25] Levine, I. N. *Quantum Chemistry*, 4th ed.: Prentice-Hall: Englewood Cliffs, NJ, 1991; Chapter 15.

[26] (a) Rutting, P. J. A.; Burgers, P. C.; Francis, J. T.; Terlouw, J. K. *J. Phys. Chem.* **1996**, *100*, 9694. (b) Arnaud, R.; Juvin, P.; Vallee, Y. *J. Org. Chem.* **1999**, *64*, 8880.

Table 4. Energetics for Sulfonyl-Transfer Reactions, Eq 4, Calculated by Various Methods with the 6-31+G* Basis Set[a] (in kcal mol^{-1})

Nu (=LG)	method	R	ΔE		ΔH	$-T\Delta S$	ΔG
F	RHF	Me	−24.49	(Int.)[c]	−26.00	8.45	−17.6
		H	−39.44	(Int.)[c]	−38.02	9.08	−28.9
		CN	−50.76	(Int.)[c]	−51.68	9.54	−42.1
	B3LYP	Me[i]	−32.05	(Int.)[c]	−32.56	7.96	−24.0
		H[i]	−44.40	(Int.)[c,i]	−45.04	8.76	−36.3
		CN[i]	−54.70	(Int.)[c]	−55.48	9.24	−46.2
	B3LYP (ext)[d]	Me	−30.35	(Int.)	−30.86	7.96	−22.9
		H	−42.36	(Int.)	−43.00	8.76	−34.2
		CN	−53.19	(Int.)	−53.97	9.24	−44.7
	SCIPCM [e]	Me	−7.00	(Int.)[c]	−7.47	7.65	0.2
		H	−17.59	(Int.)[c]	−18.23	8.79	−9.4
		CN	−24.75	(Int.)[c]	−25.50	9.23	−16.3
Cl	RHF	Me	4.51	(249i cm^{-1})[b]	4.35	7.04	11.4[h]
		H	−6.08	(315i cm^{-1})[b]	−6.46	8.07	1.6[h]
		CN	−0.16	(295i cm^{-1})[b]	−0.67	8.75	8.1[h]
	B3LYP	Me	−8.05	(118i cm^{-1})[b] (11.50)[g]	−8.06	7.21	−0.9[h]
		H	−18.69	(185i cm^{-1})[b] (172i cm^{-1})[i]	−19.08	8.07	−11.0[h]
		CN	−18.21	(71i cm^{-1})[b]	−18.70	8.65	−10.1[h]
	B3LYP (ext)[d]	Me	−6.46	(TS)	−6.47	7.21	0.7[h]
		H	−18.29	(TS)	−18.68	8.07	−10.6[h]
		CN	−17.85	(TS)	−18.34	8.65	−9.7[h]
	SCIPCM [e]	Me[f]	16.73	−	16.44	7.27	23.7[h]
		H	2.03	(242i cm^{-1})[b]	1.56	8.28	9.8[h]
		CN	2.93	(205i cm^{-1})[b]	2.39	8.86	11.3[h]

[a] Corrected for zero-point vibrational energy. The reactant energies (E, Nu = LG = Cl) for R = Me, H, and CN are −1508.92008, −1469.61080, and −1561.82662 au, respectively, at the B3LYP level. Zero-point vibrational energies were scaled by 0.9806 for B3LYP level; scaling factors are taken from Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502. RHF zero-point vibrational energies were not scaled. [b] Transition state, confirmed by only one negative eigenvalue in the Hessian matrix. [c] Intermediate, confirmed by all positive eigenvalues in the Hessian matrix. Single-well PES. [d] Calculated with extended basis sets, B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G*. [e] At the B3LYP/6-31+G* level; dielectric constant $\epsilon = 78.5$, isodensity of 0.0004 au. This ΔE value includes solvation energies, ΔG_s. [f] Adduct failed to converge. The electronic energy is calculated by using the gas-phase geometry, and thermal energy data are taken from the gas-phase results. [g] The intrinsic barrier, $\Delta E^{\ddagger}_0 = \Delta E^{\ddagger} - \Delta E$(RC). [h] The $\Delta G^{\ddagger}$ values based on the separated reactants level. [i] Confirmed at the B3LYP/6-311+G(3df,2p) level.

Table 5. Energetics for Sulfinyl-Transfer Reactions, Eq 5, Calculated by Various Methods with the 6-31+G* Basis Set[a] (in kcal mol^{-1})

method	R	ΔE		ΔH	$-T\Delta S$	ΔG
RHF	Me	−14.12	(75i cm^{-1})[b]	−14.53	7.56	−7.0
	H	−20.49	(Int.)[c]	−20.41	5.33	−15.1
	CN	−23.01	(Int.)[c]	−23.01	6.90	−16.1
B3LYP	Me	−25.86	(Int.)[c]	−25.93	6.89	−19.0
	H	−30.86	(Int.)[c,i] (2.59)[g]	−30.99	6.71	−24.3 (−19.0)[h]
	CN	−36.43	(Int.)[c]	−36.53	7.14	−29.4[j]
B3LYP (ext)[d]	Me	−24.31	(Int)	−24.38	6.89	−17.5
	H	−29.55	(Int)	−29.68	6.71	−23.0
	CN	−35.59	(Int)	−35.69	7.14	−28.6
SCIPCM[e]	Me [f]	−5.41	−	−5.52	6.95	1.4
	H	−10.09	(Int.)[c]	−10.22	6.79	−3.4 (1.6)[h,k]
	CN[f]	−13.21	−	−13.34	7.21	−6.1

[a] Corrected for zero-point vibrational energy. The reactant energies (E) for R = Me, H, and CN are −1433.72289, −1394.41702, and −1486.64038 au, respectively, at the B3LYP level. Zero-point vibrational energies were scaled by 0.9806 for the B3LYP level; scaling factors are taken from Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502. RHF zero-point vibrational energies were not scaled. [b−g]Same as Table 4. [h] $\Delta G^{\ddagger}$ values based on the separated reactants. [i] Confirmed at the B3LYP/6-311+G(3df,2p) level. [j] Single-well PES. [k] $\Delta G^{\ddagger}_{\mathrm{sol}} = \Delta G^{\ddagger}(\mathrm{gas}) + \delta\Delta G^{\ddagger}_{\mathrm{s}}$, where $\delta\Delta G^{\ddagger}_{\mathrm{s}} = \Delta G^{\ddagger}_{\mathrm{s}} - \Delta G_{\mathrm{s}}(\mathrm{React.})$; $\Delta G^{\ddagger}_{\mathrm{s}}$ and $\Delta G_{\mathrm{s}}(\mathrm{React.})$ are the solvation energies for transition state and reactants respectively, which are calculated at the SCIPCM/B3LYP/6-31+G*//B3LYP/6-31+G* level.

more positive ($\Delta q_{(S)} = -0.027$ and $\Delta q_{(O)} = +0.005$ au for R = H) upon adduct formation in the sulfonyl transfer, which is exactly opposite to the case for more positive S and more negative O in the sulfinyl transfer ($\Delta q_{(S)} = +0.008$ and $\Delta q_{(O)} = -0.045$ au for R = H), in agreement with the sulfinyl S═O being more polarizable and weaker than the sulfonyl S═O bond. This comparison of charge shifts upon adduct formation is similar to that between carbonyl and thiocarbonyl transfers (vide supra); the thiocarbonyl group is much more polarizable and more prone to react by a stepwise mechanism through an intermediate.

Our results on the sulfinyl transfers show that stretching of S−Cl is ca. 45% and that of S═O is ca. 1.0% in a distorted TBP-5C TS formed with an equatorial lone pair of the sulfur atom.

The energetics of sulfonyl and sulfinyl group transfers are summarized in Tables 4 and 5, respectively. For the fluoride, F$^-$, nucleophile (and also leaving group) in the sulfonyl (**III**) and all of the sulfinyl (**IV**) transfers, the reactions proceed with distorted TBP-5C adducts as intermediates, whereas for sulfonyl transfers with the chloride, Cl$^-$, nucleophile the adducts are TSs in double-well-type PESs. We note that the well depths for F$^-$ exchanges are quite deep, indicating that the TBP-5C adducts are stable intermediates, which of course is due to a strong S−F bond; i.e., the leaving group (F$^-$) expulsion from the intermediate requires high energy. It is also true that the $\sigma^*_{\mathrm{S-F}}$ level (0.156 au for R = H) is much higher than the $\sigma^*_{\mathrm{S-Cl}}$ level (0.096 au for R = H) due to the stronger electronegative F, so the energy gap, $\Delta\epsilon = \epsilon(\sigma^*) - \epsilon(\pi^*)$, is much greater than the corresponding $\Delta\epsilon$ for chloride exhanges.[13] The B3LYP TSs for Cl$^-$ exchanges are below the level for the separate reactants in the gas phase in most cases (except for R = Me in the B3LYP/6-311+G(3df,2p) result), but the TSs are predicted to rise above the reactant level in water.

Experimentally, many examples of concerted (S$_N$2) displacement reactions at the sulfonyl sulfur are reported in solution.[27] The stepwise sulfonyl transfers for fluoride are in line with the generally accepted view that acyl transfers between a strong nucleophile (donor) and a weak nucleofuge (acceptor) are more prone to a stepwise reaction through an intermediate.[3h]

An important requirement for the stepwise mechanism through an intermediate is that the acyl X═Y (S═O in this case) π bond is weaker than the bond to the leaving group.[28] As discussed above, the sulfinyl group (S═O) is partially polarized in the reactant state due to the relatively low-lying $\pi^*_{\mathrm{S=O}}$ levels, so the π bond must be much weaker than the S−Cl σ bond. In contrast, the sulfonyl S═O bonds are less polarizable than the sulfinyl S═O bond, so the S═O π bond must be stronger than the sulfinyl S═O. In the fluoride exchanges of the sulfonyl system, the bond strength of S−F should be much greater than that of the S═O π bond, and so a stepwise mechanism through an intermediate is predicted. The sulfinyl $\pi^*_{\mathrm{S=O}}$ level is substantially lower (0.014 au for R = H) than the sulfonyl $\pi^*_{\mathrm{S=O}}$ (0.027 au for R = H), so intermediate formation is energetically easier in the sulfinyl than sulfonyl transfers. This may be the reason why the sulfinyl group transfers between Cl$^-$ are predicted to proceed via an intermediate in the gas phase as

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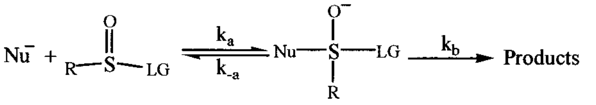
(27) Gordon, I. M.; Maskill, H.; Ruasse, M.-F. *Chem. Soc. Rev.* **1989**, *18*, 123.

(28) Reference 1a, Chapter 7, and ref 1b, Chapter 4.

well as in solution (water) in Tables 4 and 5. A common feature that is conducive to the stepwise mechanism for thiocarbonyl (**II**) and sulfinyl (**IV**) is clearly the low $\pi^*_{X=Y}$ level, which ensures a facile access of the nucleophile to the acyl functional center to form a stable adduct. It is also notable that the well depth for the sulfinyl transfers becomes deeper, i.e., the stability of the intermediate increases, with an increase in the electron-withdrawing power of R, $-17.5 \rightarrow -23.0 \rightarrow -28.6$ kcal mol^{-1} for R = Me → H → CN, but the barrier height (the TS) in the concerted sulfonyl-transfer process becomes elevated slightly with R = CN, $0.8 \rightarrow -10.6 \rightarrow -9.7$ kcal mol^{-1} for R = Me → H → CN. Furthermore, the $\Delta G^‡$ (and $\Delta E^‡$) values for the sulfonyl transfers in Table 4 show that the value for R = CN (-10.1 kcal mol^{-1} at the B3LYP level) is practically the same as that for R = H (-11.0 kcal mol^{-1}), which is in contrast to a large lowering of the $\Delta G^‡$ values (by ca. -5 to -10 kcal mol^{-1}), accompanied by the change of R from H to CN in other group transfers. This odd behavior of R = CN in the sulfonyl transfer can be rationalized as being due to the compensating effect of the π-donor ability of R = CN under the high electron demand of strong electron-acceptor groups,[29] the two oxygens in the equatorial (or radial) positions in the TBP-5C adduct; the three equatorial groups, the two oxygens and a CN, attached to the central S atom can interact inductively (CN acts as a σ acceptor) as well as conjugatively (CN acts as a π donor). This type of effect is, in fact, possible only in the TBP-5C adduct for the sulfonyl transfer since the three equatorial groups, R = CN and two oxygens, are almost coplanar with the central S atom. This coplanarity in the TBP-5C adduct ensures maximum overlap of the π-orbitals of the four groups (or atoms) on the equatorial plane. In the TBP-5C adduct involved in the sulfinyl transfer, an equatorial lone pair acts as a σ donor (not an acceptor), so the CN group cannot play the role of a π donor. These trends in the gas phase remain unchanged in solution (Tables 4 and 5).

The most direct experimental evidence for a concerted sulfonyl group transfer in solution was provided by the application of the quasi-symmetrical technique to the reactive oxyanions (RO^-) with 4-nitrophenyl 2,4-dinitrobenzenesulfonate ($2,4\text{-}(NO_2)_2{\cdot}C_6H_3{\cdot}SO_2{\cdot}C_6H_5{-}NO_2$).[30] A linear plot was obtained for the Brønsted-type plot of $\log(k_{RO})$ versus the pK_a of the alcohol (p$K_{a(ROH)}$) over a pK_a range at least 2 units above and below the pK_a of the leaving group, 4-nitrophenolate anion. There are other S_N2-type reactions of sulfonyl transfers in solution.[27,31] Although sulfonyl transfer is usually discussed in terms of a concerted displacement,[27] an example of a stepwise process in which a TBP intermediate with a hypervalent sulfur is formed has been presented.[32] Strongly electron-withdrawing substituents are reported to be conducive to such a stepwise sulfonyl transfer.[32]

The paucity of reported kinetic data on the sulfinyl group transfer prevents us from making any fruitful comparative discussion. In the preparation of a sulfinate ester, the sulfinyl chloride reacts with an aliphatic or aromatic alcohol in the presence of base. This reaction, once thought to proceed via an S_N2 mechanism, is now generally accepted to involve a sulfurane intermediate.[33] The successful preparation of many sulfuranes and related compounds supports the contention that stable TBP-type adducts (TBP(SO)) are energetically feasible and should be able to exist as we theoretically predicted in the present work. However, attempts to demonstrate their presence have met with rather limited success, and the mechanism of the sulfinyl group transfer, i.e., whether the adduct is a TS or an intermediate, has long been controversial.[33,34] Although the original authors did not realize it,[35] a biphasic dependence of the rates on the basicity (pK_a) of nucleophiles in the reactions of alkoxides and phenoxides with aryl methanesulfinates ($CH_3S(=O)OAr$) clearly indicated a mechanistic changeover from a breakdown ($\beta_{nuc} = 0.79$) to formation ($\beta_{nuc} \cong 0.0$) of TBP intermediate as the basicity of the nucleophile (aryloxides) is increased. The relatively large magnitude of the Brønsted coefficient for the leaving group variation, β_{lg} ($\cong -0.71$), also supported the stepwise mechanism through a stable intermediate.[4a,b] The pK_a°, at which the rates of the two leaving groups from the putative intermediate are equal, $k_{-a} = k_b$ in eq 6, corresponded ca. p$K_a \cong 11$, which is also quite reasonable.[4a,b] We think that this is a rare example of the sulfinyl-group-transfer reaction, which has been shown kinetically to proceed by a stepwise mechanism with rate-limiting expulsion of the LG from a stable intermediate.



$$\mathrm{Nu^-} + \mathrm{R}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}-\mathrm{LG} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \mathrm{Nu}-\overset{\mathrm{O^-}}{\overset{|}{\underset{\underset{\mathrm{R}}{|}}{\mathrm{S}}}}-\mathrm{LG} \xrightarrow{k_b} \textbf{Products} \qquad (6)$$

The reactions of sulfinyl chlorides with oxygen or nitrogen nucleophiles are reported to proceed extremely rapidly below room temperature in good yields.[33b] The lowest $\pi^*_{S=O}$ levels (Table 3) and the reaction barriers (compare $\Delta G^‡$ in Tables 1, 2, 4, 5, and 6) for the sulfinyl transfers are thus in general agreement with the experiments.

The barriers to adduct formation by Cl^- at sulfonyl centers in Table 4 are higher than those for sulfinyl centers in Table 5. This is consistent with the preferential sulfinyl attack by soft nucleophiles (I^-, Br^-, Cl^-, etc.) in the nucleophilic reactions of diaryl sulfinyl sulfones, $RSO{-}SO_2{-}R$, in solution.[34,36] The sulfinyl sulfur is reported to be "softer" than the sulfonyl sulfur, so a relatively softer nucleophile, Cl^-, should prefer to attack the sulfinyl center.[36]

(C) Identity Phosphoryl Group (V; $(RO)_2PO-$) Transfers.

In this work, we chose one of the most important biological phosphyl groups, the neutral phosphoryl group, $(RO)_2PO-$. The

$$\mathrm{Cl^-} + (\mathrm{RO})_2-\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}-\mathrm{Cl} \rightleftharpoons \mathrm{Cl}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}-(\mathrm{OR})_2 + \mathrm{Cl^-} \qquad (7)$$

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(29) (a) Taagepera, M.; Summerhays, K. D.; Hehre, W. J.; Topsom, R. D.; Pross, A.; Radom, L.; Taft, R. W. *J. Org. Chem.* **1981**, *46*, 891. (b) Gassman, P. G.; Jalley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 1214. (c) Lee, I.; Kim, C. K.; Han, I. S.; Lee, H. W.; Kim, W. K.; Kim, Y. B. *J. Phys. Chem. B* **1999**, *103*, 7302. (d) Paddon-Row, M. N.; Santiago, C.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6561. (e) Dixon, D. A.; Eades, R. A.; Frey, R.; Gassman, P. G.; Hendewerk, M. L.; Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 3885. (f) Dixon, D. A.; Charlier, P. A.; Gassman, P. G. *J. Org. Chem.* **1984**, *49*, 3959. (g) El-Nahasand, A. M.; Clark, T. *J. Org. Chem.* **1995**, *60*, 8023.

(30) D'Rozario, P.; Smyth, R. L.; Williams, A. *J. Am. Chem. Soc.* **1984**, *106*, 5027.

(31) (a) Lee, I.; Koo, I. S. *Tetrahedron* **1983**, *39*, 1803. (b) Lee, I.; Shim, C. S.; Chung, S. Y.; Kim, H. Y.; Lee, H. W. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1919.

(32) Baxter, N. J.; Rigoreau, L. J. M.; Laws, A. P.; Page, M. I. *J. Am. Chem. Soc.* **2000**, *122*, 3375.

(33) (a) Fernandez, I.; Khiar, N.; Llera, J. M.; Alcudia, F. *J. Org. Chem.* **1992**, *57*, 6789. (b) Schwan, A. L.; Strickler, R. R. *Org. Prep. Proced.* **1999**, *31*, 579. (c) Bravo, P.; Zanda, M.; Zappala, C. *Tetrahedron Lett.* **1996**, *37*, 6005.

(34) Tillet, J. G. *Chem. Rev.* **1976**, *76*, 747.

(35) Senatore, L.; Ciuffarin, E.; Fava, A.; Levita, G. *J. Am. Chem. Soc.* **1973**, *95*, 2918.

(36) Kice, J. L.; Guaraldi, G. *J. Am. Chem. Soc.* **1967**, *89*, 4113.

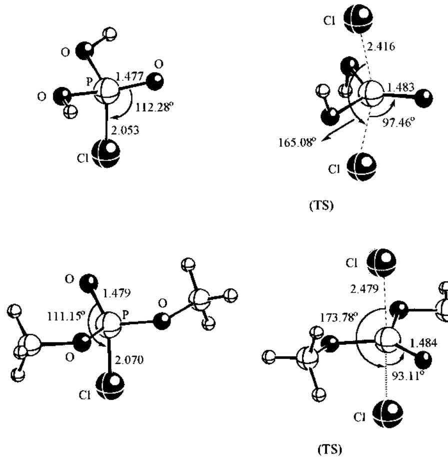

Figure 3. Structures of reactants and adducts for phosphoryl-transfer reactions with Nu = LG = Cl^-, calculated at the B3LYP/6-31+G* level (bond lengths in angstroms, and angles in degrees).

Table 6. Energetics for Phosphoryl Transfers, Eq 7, Calculated by Various Methods with the 6-31+G* Basis Set[a] (in kcal mol^{-1})

method	R	ΔE		ΔH	$-T\Delta S$	ΔG_g
RHF	Me	11.91	(291i cm^{-1})[b]	11.58	8.13	19.7
	H	3.70	(285i cm^{-1})[b]	2.72	9.89	12.6
B3LYP	Me	1.52	(152i cm^{-1})[b]	1.06	8.78	9.8
	H	−10.53	(135i cm^{-1})[b] (31.55)[c] (151i cm^{-1})[d]	−11.42	9.56	−1.9
B3LYP (ext)[e]	Me	1.53		1.07	8.78	9.9
	H	−10.93		−11.82	9.56	−2.3
SCIPCM[f]	Me	20.05		19.59	8.78	28.4
	H	12.80		11.91	9.56	21.5

[a] Corrected for zero-point vibrational energy. The reactant energies (E) for R = Me and H are −1567.31410 and −1488.75917 au, respectively, at the B3LYP level. Zero-point vibrational energies were scaled by 0.9806 for the B3LYP level; scaling factors are taken from Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502. RHF zero-point vibrational energies were not scaled. [b] Transition state, confirmed by only one negative eigenvalue in the Hessian matrix. [c] The intrinsic barrier, $\Delta E^{\ddagger}_{o} = \Delta E^{\ddagger} - \Delta E(\mathrm{RC})$. [d] Confirmed at the B3LYP/6-311+G(3df,2p) level. [e] Electronic energies were calculated with extended basis sets at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G* level. [f] Single-point calculations using gas-phase geometries (i.e., SCIPCM/B3LYP/6-31+G*//B3LYP/6-31+G* level) with the dielectric constant $\epsilon = 78.5$ and isodensity of 0.0004 au. This ΔE values includes solvation energies, ΔG_s. Thermal energy data were taken from the gas-phase results.

importance of phosphorus chemistry stems from its relevance to biological chemistry and from its usefulness in synthesis.[1,37]

The reactant, phosphoryl chloride, has a tetrahedral structure, but the adduct, $(RO)_2POCl_2^-$, is a distorted TBP-5C type (Figure 3). The stretching of the P=O bond upon adduct formation (Tables S12 and S13, Supporting Information) is small, $\Delta d_{P=O} = 0.006$ Å (for R = H), which is similar to or slighter greater than that of the S=O bond in the sulfonyl group transfers ($\Delta d_{S=O} = 0.004$ Å for R = H). The two apical Cl and P atoms are nearly collinear, with $\angle$Cl−P−Cl $\cong$ 165° and 174° for R = H and CH_3, respectively. The P−Cl bond (2.053 Å for R = H) is shorter than the S−Cl bonds in the sulfonyl (2.100 Å for R = H) as well as in the sulfinyl (2.178 Å for R = H) system, and hence the P−Cl bond should be stronger than the S−Cl bond (vide infra).

The energetics in Table 6 reveal that the phosphoryl transfers are predicted to proceed via a double-well PES in the gas phase (or by a concerted mechanism with a TBP-5C TS in solution). The bond stretching of P−Cl was ca. 45% and that of P=O was ca. 2% at the TS.

It has been shown experimentally that the phosphoryl transfer between nucleophiles is closely similar to those of the sulfonyl series.[1] Indeed, the two transfers (**III** and **V**) involve double-well PESs (concerted), and the TS is reached with ca. 45% change of X−Cl (X = S or P) stretching with a very small change (ca. 1%) of X=Y distance in a distorted TBP-5C TS structure. The TSs for the two transfer reactions are stabilized by the relatively strong proximate charge-transfer interactions ($-\sum\Delta E_{\sigma-\sigma^*} \cong 120-500$ kcal mol^{-1}) and stabilizing electrostatic interactions ($\sum\Delta E_{es} \cong -10$ to -45 kcal mol^{-1}).

However, the barrier heights are higher by ca. 8−9 kcal mol^{-1} than the corresponding sulfonyl group transfers (Table 4) in the gas phase (and by ca. 5−10 kcal mol^{-1} in water). The greater bond strength of P−Cl (79 kcal mol^{-1}) than S−Cl (67 kcal mol^{-1})[38] could be a reason for the higher barriers of phosphoryl than of sulfonyl transfers. For both R = CH_3 and H, the $\pi^*_{P=O}$ and σ^*_{P-Cl} levels are relatively high (higher than those for sulfonyl), but the energy gap, $\Delta\epsilon$, is relatively small (smaller than those for carbonyl and thiocarbonyl group transfers, Table 3), which is in line with the double-well PES (concerted mechanism) predicted. The predicted (concerted) mechanism for the phosphoryl group transfer is consistent with the experimental results obtained in aqueous solution, in which the phosphoryl group transfer involves usually a concerted mechanism.[1,39] Linear Brønsted plots are obtained for the attack of aryloxyanions (ArO^-) on the 4-nitrophenyl ester of the diphenyl phosphate and diphenylphosphinate, demonstrating concerted transfer of a neutral phosphoryl group between weakly basic nucleophiles in aqueous solution.[40] The aminolyses of diphenyl chlorophosphates with anilines and pyridines in acetonitrile are also shown to proceed concertedly.[41] However, it is known that phosphoryl group transfers between strong donor and acceptor nucleophiles such as alkoxide ions prefer to proceed via a TBP-5C intermediate.[1a,42] Since Cl^- is a weak nucleophile, our DFT results for the concerted (double-well PES) mechanism are in line with the experiment.

(D) General Discussion. It has been shown that standard G1 and G2 calculations on hypervalent sulfur-containing molecules lead to inaccurate heat of formation due to the inadequate basis set (6-31G*) that was used for geometry optimization.[26a] For reliable equilibrium structures, larger split-valence basis sets, e.g., 6-311+G(2df, 2p), are required. The best agreement with experimental results is achieved when one uses an f function on heavy atoms, and the geometry calculated at the B3LYP/6-311+G(3df,2p) level was found to be very close to the experimental one.[26b] We therefore recharacterized the adducts formed in the sulfonyl-, sulfinyl-, and phosphoryl-transfer reactions (with R = H) at the B3LYP/6-311+G(3df,2p) level and confirmed that the nature of adducts (TS or intermediate) predicted by characterization at the B3LYP/6-31+G* level is correct (Tables 4−6).

In the discussion presented above, we have dealt only with the out-of-plane attack of the X=Y π bond ($S_N\pi$ path).

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[37] (a) Thatcher, G. R. J.; Kluger, R. *Adv. Phys. Org. Chem.* **1989**, *25*, 99. (b) Williams, A. *Acc. Chem. Res.* **1989**, *22*, 387.

[38] Sanderson, R. T. *Chemical Bonds and Bond Energy*; Academic Press: New York, 1971; p 154.

[39] Kice, J. L. *Adv. Phys. Org. Chem.* **1980**, *17*, 65.

[40] (a) Ba-Saif, S. A.; Waring, M. A.; Williams, A. *J. Am. Chem. Soc.* **1990**, *112*, 8115. (b) Ba-Saif, S. A.; Waring, M. A.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1653. (c) Waring, M. A.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1742. (d) Bourne, N.; Chrystiuk, E.; Davis, A. M.; Williams, A. *J. Am. Chem. Soc.* **1988**, *110*, 1890.

[41] (a) Guha, A. K.; Lee, H. W.; Lee, I. *J. Org. Chem.* **2000**, *65*, 12. (b) Guha, A. K.; Lee, H. W.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1999**, 765.

[42] Hudson, R. F.; Brown, C. *Acc. Chem. Res.* **1972**, *5*, 204.

However, it may also be possible that the nucleophile attacks at the back side of the X−Cl σ bond ($\mathrm{S_N}\sigma$ path). For the carbonyl and thiocarbonyl transfers, the σ-attack occurs within the molecular plane, i.e., an in-plane σ-attack. This type of in-plane σ-attack ($\mathrm{S_N}\sigma$) pathway has been shown to be actually preferred to the out-of-plane π-attack ($\mathrm{S_N}\pi$ path) in the nucleophilic substitution at unactivated vinylic carbon.[19,43] However, as we have shown earlier,[3h] the nucleophilic substitution at the carbonyl carbon occurs only through an $\mathrm{S_N}\pi$ path; the $\mathrm{S_N}\sigma$ pathway not only is unfeasible (a saddle point with only one imaginary frequency was often not obtainable) but also constituted a much higher barrier path. This difference in the mechanism between vinyl and carbonyl transfers appears to arise from the difference in the level of $\sigma^*_{\mathrm{C-Cl}}$. In the vinyl transfer, the $\sigma^*_{\mathrm{C-Cl}}$ level is higher by only 0.017 au (at the RHF/6-311+G**//RHF/6-311+G** level) than the $\pi^*_{\mathrm{C=C}}$ level, in contrast to a much larger $\sigma^*-\pi^*$ gap of 0.051 au (at the RHF/6-31+G*//B3LYP/6-31+G* level) for the carbonyl transfer. Furthermore, the major factor conducive to the preference of an $\mathrm{S_N}\sigma$ path for vinyl chloride reactions with $\mathrm{Cl^-}$ and $\mathrm{Br^-}$ nucleophiles was a *strong stabilizing electrostatic interaction* in addition to a low exclusion repulsion in a loose TS with a large degree of bond cleavage ($\%\Delta n^\ddagger_{(\mathrm{C-Cl})} \cong 65$).[19b] For the carbonyl (and thiocarbonyl) transfers, the percentage bond order changes of the C−Cl bond in the TS are lower (34−44%) in the relatively tight TSs. In other acyl group transfers investigated in the present work, the smallest $\pi^*-\sigma^*$ level gap is 0.051 au, and the gaps are, in general, much greater than this (0.07−0.13 au), so the $\mathrm{S_N}\sigma$ path was not found to be viable (for **I**, **II**, **III**, and **V**) or at least cannot compete with the $\mathrm{S_N}\pi$ pathway (for the sulfinyl (**IV**) transfer, which involves a relatively low $\sigma^*_{\mathrm{S-Cl}}$ level, the $\Delta E^\ddagger(\mathrm{R = H})$ for the $\mathrm{S_N}\sigma$ path, which had C_{2v} symmetry with two imaginary frequencies, 1822i and 43i cm^{-1}, is higher by ca. 73 kcal mol^{-1} than that for the corresponding $\mathrm{S_N}\pi$ path), according to our exploratory computational results for the selected reactions. We therefore conclude that, in order for the $\mathrm{S_N}\sigma$ path to be preferred over, or competitive with, the $\mathrm{S_N}\pi$ pathway, *availability of a low-lying* σ^*_{X-LG} *orbital is essential*. The low-energy $\sigma^*_{\mathrm{X-LG}}$ orbital should be as low as possible (with a narrow $\pi^*-\sigma^*$ gap), preferably below the $\pi^*_{\mathrm{X=Y}}$ level,[19b,43] so that the HOMO of nucleophile ($\mathrm{n_N}$) can interact with the $\sigma^*_{\mathrm{X-LG}}$ orbital with an energy gain that is greater than, or similar to, that for the interaction with the $\pi^*_{\mathrm{X=Y}}$ orbital. When the nucleofugality of the leaving group (LG) is strong enough, as in the case of $\mathrm{Cl^-}$ and $\mathrm{Br^-}$, the incipient $\mathrm{n_N}-\sigma^*_{\mathrm{X-LG}}$ interaction may lead to an extensive bond cleavage in a loose TS. For the sulfonyl, sulfinyl, and phosphoryl transfers with the TBP adducts, the electrostatic energy changes are stabilizing ($\Delta E_{\mathrm{es}} < 0$), in contrast to the destabilizing interaction energy changes ($\Delta E_{\mathrm{es}} > 0$) in the carbonyl and thiocarbonyl transfers with the tetrahedral adducts (Table S3). However, the stabilizing energy changes in the TBP adduct formation are relatively small.

Examination of the activation barriers, $\Delta G^\ddagger$ (and $\Delta E^\ddagger$), reveals that the barrier heights are much lower for the sulfonyl and sulfinyl transfers than for other group transfers (Tables 1, 2, 4, 5, and 6); for R = H, the $\Delta G^\ddagger$ increases in the order RSO (−23.0) ≪ $\mathrm{RSO_2}$ (−10.6) < RCO (−3.0) ≤ RCS (−2.5) ≤ $\mathrm{(RO)_2PO}$ (−2.3 kcal mol^{-1}). The much lower barriers to sulfonyl and sulfinyl transfers are again related to the lower $\pi^*_{\mathrm{X=Y}}$ and $\sigma^*_{\mathrm{X-Cl}}$ levels in Table 3. It is notable that both antibonding levels (π^* and σ^*) are the lowest for the sulfinyl transfers for which the barrier heights are the lowest. The reactivity of the acyl group transfer is therefore dependent on both the $\pi^*_{\mathrm{X=Y}}$ and $\sigma^*_{\mathrm{X-LG}}$ levels. The lower the levels of both the $\pi^*_{\mathrm{X=Y}}$ and $\sigma^*_{\mathrm{X-LG}}$ orbitals, the greater is the reactivity of the acyl-group-transfer reactions.

The gas-phase well depths, $\delta\Delta G_{\mathrm{wd}} = \Delta G^\ddagger - \Delta G_{\mathrm{Int}}$, are in general shallow, so the transition structure regions are flat.[44] The $\delta\Delta G_{\mathrm{wd}}$ values in the sulfinyl transfers (ca. 5 kcal mol^{-1}) are greater than those for the thiocarbonyl transfers (ca. 1 kcal mol^{-1}). This is a manifestation of the greater $\mathrm{n_N}-\pi^*$ charge-transfer energies[9,13] for the former due to the lower $\pi^*_{\mathrm{S=O}}$ than $\pi^*_{\mathrm{C=S}}$ levels (except for R = CN, for which single-well PESs are found).

Since the reactions investigated in this work are all thermoneutral ($\Delta G^\circ = 0$), the $\Delta G^\ddagger$ (and $\Delta E^\ddagger$) values are the intrinsic barriers, $\Delta G^\ddagger_{\mathrm{o}}$ (and $\Delta E^\ddagger_{\mathrm{o}}$), and the Marcus theory[45] predicts that the position of the TS, α in eq 8, is ideally 0.5, i.e., the TS should occur at 50% progress of the reaction along the reaction coordinate. However, the percentage bond order changes of the

$$\alpha = \frac{1}{2} + \frac{\Delta G^\circ}{8\Delta G^\ddagger_{\mathrm{o}}} \tag{8}$$

X−Cl bond stretching ($\%\Delta n^\ddagger_{(\mathrm{X-Cl})}$) are ca. 32−45% (B3LYP) for the reactions involving tetrahedral adducts (for **I** and **II**) but are ca. 44−49% for the reactions proceeding through TBP-5C adducts (**III**−**V**). The lower degree of C−Cl bond cleavage in the adduct of carbonyl (**I**) and thiocarbonyl (**II**) transfers may also be due to the higher $\sigma^*_{\mathrm{C-Cl}}$ levels of **I** (0.235 au) and **II** (0.209 au) than those of **III** (0.096 au), **IV** (0.095 au), and **V** (0.175 au). The higher the σ^* level, the smaller are the second-order $\mathrm{n_N}-\sigma^*$ charge-transfer interaction energies,[9,13] i.e., the harder it is to break the X-Cl bond, and hence the adduct is formed at less than 50% progress of the reaction. In the tetrahedral adduct the $\pi^*_{\mathrm{C=Y}}$ and $\sigma^*_{\mathrm{C-Cl}}$ orbitals make a ca. 40° angle[3e,46] (Figure 1), so the overlap (i.e., mixing) between the two is ca. 0.77 (cos 40°) times that of the maximum possible. In contrast, in the TBP adduct, the two orbitals are parallel, and maximum overlap (mixing) is possible. This could be a possible cause for the lower degree of C−Cl bond breaking than P−Cl and S−Cl bond cleavage in the adduct formation.

The low π^* levels for **II** ($\pi^*_{\mathrm{C=S}}$) and **IV** ($\pi^*_{\mathrm{S=O}}$) have several consequences on the equilibrium and dynamic properties of the group-transfer reactions: (i) The energy lowering by incorporation of the electron correlation effect, $\delta\Delta E^\ddagger_{\mathrm{corr}} = \Delta E^\ddagger(\mathrm{B3LYP}) - \Delta E^\ddagger(\mathrm{RHF})$, is related to the delocalization of π bonds.[9] The greater the delocalization of π-electron, the larger is the energy lowering by accounting for the correlation effect. We note that the energy lowering, $\delta\Delta E^\ddagger_{\mathrm{corr}}$, is relatively small in the adduct formation for the thiocarbonyl (−7.6) and sulfinyl (−10.4 kcal mol^{-1} for R = H) transfers compared to those for the carbonyl (−15.8), sulfonyl (−12.6), and phosphoryl (−14.2 kcal mol^{-1}) transfers. This is consistent with the strong contribution of dipolar structures in the initial states of **II** and **IV**; i.e., due to the low π^* levels, the π bonds are already partially broken in the reactant state, so the changes in correlation energy upon adduct formation should be small. (ii) The weaker $\pi_{\mathrm{X=Y}}$ bonds

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(43) Lucchini, V.; Modena, G.; Pasquato, L. *J. Am. Chem. Soc.* **1995**, *117*, 2297.

(44) Lee, I.; Kim, C. K.; Li, H. G.; Lee, B.-S.; Lee, H. W. *Chem. Phys. Lett.* **2000**, *320*, 307.

(45) Pross, A. *Theoretical and Physical Principles of Organic Reactivity*; Wiley: New York, 1995; Chapter 5.

(46) The adducts in Figure 1 show that the RCO plane bisecting the Cl−C−Cl angle (∼100°) leads to ∠OCCl ≅ 130°, so the $\pi^*-\sigma^*$ angle is ca. 40°.

for **II** and **IV** lead to lower intrinsic barriers, $\Delta E_o^\ddagger$, than for other group (**I**, **III**, and **V**) transfers, which is again a manifestation of the lower $\pi^*_{X=Y}$ levels for **II** and **IV**. (iii) Solvation stabilization, $\Delta G_o^\ddagger$, is greater for the more polarized adducts of **II** and **IV**. (iv) The proximate charge-transfer energies ($-\sum\Delta E^{(2)}_{\sigma-\sigma^*}$) are smaller for **II** (14−66) and **IV** (68−158 kcal mol^{-1}) than for **I** (160−574), **III** (116−359), and **V** (426−498 kcal mol^{-1}). This could also result from the low π-bond order involved in the adducts of **II** and **IV**.[9] (v) The electrostatic interaction energy changes, ΔE_{es}, involved in the adduct formation are destabilizing for **II** and **IV** due to the strong repulsive interactions between negative charges on the two Cl and strongly polarized S and O atoms, respectively.

The deformation energies,[17] $\Delta E^\ddagger_{def}$, defined as the difference in the energies of the reactant (acyl compound) and the adduct structure (devoid of the nucleophile, Cl$^-$) involved in the sulfonyl (and sulfinyl) and phosphoryl group transfers (30−47) are only slightly higher than those for the carbonyl and thiocarbonyl group transfers (27−37 kcal mol^{-1}). Since in the former the TBP-5C adducts are formed, the central atoms, S and P, involve hybridization changes from sp^3 to sp^{3}d. In contrast, in the latter group transfers, hybridization of the central carbon changes from sp^2 to sp^3 in the adduct formation. The %$\Delta n^\ddagger$ values for the C−Cl bond in the tetrahedral adduct formation of **I** and **II** are ca. 32−45% (B3LYP), whereas those for the S−Cl (ca. 44−49%) and P−Cl (ca. 46−48%) bond in the TBP-5C adduct formation are somewhat greater. Since the major component of the $\Delta E^\ddagger_{def}$ is known to be the stretching of the X−LG bond,[17] the $\Delta E^\ddagger_{def}$ in the TBP-5C adduct formation is expected to be greater than that in the tetrahedral adduct formation on account of the greater X−LG bond stretching alone. The fact that the deformation energies found for the TBP-5C adduct formation are only slightly greater (by less than 10 kcal mol^{-1}), despite the greater stretching of P−Cl, suggests that participation of d-orbitals in the TBP-5C adduct formation does not require any significant additional energy. This is in line with the theory of hypervalency involving the d-orbitals such that central atom sp^{3}d or sp^{3}d^2 hybridization is irrelevant to the nature of the chemical bonding of the hypervalent molecule.[47] The experimental and theoretical evidence indicated that d orbitals are not qualitatively important in the hypervalency of second-row atoms, and they are in fact not essential for the general phenomenon of hypervalency.[48]

(E) Summary and Conclusion. We can summarize the results of the present studies on the identity group transfers, Cl$^-$ + R(X=Y)Cl, as follows. In the gas-phase carbonyl group transfers, the single- or triple-well PES (the stepwise mechanism) is observed only when a strong electron-withdrawing group is attached to the functional center, R = CN, since the acceptor R depresses more the $\pi^*_{C=O}$ level than the σ^*_{C-Cl} level so that the energy gap, $\Delta\epsilon = \epsilon(\sigma^*) - \epsilon(\pi^*)$, is widened. For the thiocarbonyl group transfers, the $\pi^*_{C=S}$ is much lower than the $\pi^*_{C=O}$ level, and hence the possibility of the thiocarbonyl group transfer proceeding through a single- or triple-well PES becomes greater than that of the carbonyl group transfer. The sulfonyl and phosphoryl group transfers proceed via a double-well PES (concertedly) due to relatively high $\pi^*_{X=Y}$ ($\pi^*_{S=O}$ and $\pi^*_{P=O}$) levels. However, the identity sulfonyl group transfers between fluorides, (F$^-$ + RSO$_2$F), are predicted to react through an intermediate (by a stepwise mechanism) due to the strong S−F bond, which is in turn due to the high σ^*_{S-F} level. On the other hand, the sulfinyl group transfers are predicted to take place through an intermediate due mainly to the weak S=O π bond, which is a result of the low $\pi^*_{S=O}$ level. We therefore conclude that the major factors that are in favor of a reaction through an intermediate are the low $\pi^*_{X=Y}$ and high σ^*_{X-LG} levels. A stronger electron-acceptor R group and a worse nucleofuge, LG, attached to the functional center, X, are more conducive to the stepwise mechanism through an intermediate due to a greater lowering of the $\pi^*_{X=Y}$ level and a greater elevation of the σ^*_{X-LG} level, respectively. The reactivity of an acyl group transfer is also dependent on the π^* and σ^* levels; the lower the levels of both π^* and σ^* orbitals, the greater is the reactivity. For the backside σ-attack acyl transfer to be feasible, availability of a low-lying σ^*_{X-LG} orbital is essential, and the σ^*_{X-LG} level should be preferably below the $\pi^*_{X=Y}$ level. Polar solvent raises the activation barriers almost uniformly, so the relative gas-phase order of $\Delta G^\ddagger$ among the different R groups remains unchanged.

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Supporting Information Available: Tables of selected geometrical parameters, reactant structures and complexation energies, electrostatic, deformation, and interaction energies, solvation energies, NBO charges, eleectronic energies, and *Z*-matrices (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(47) Reed, A. E.; Weinhold, F. *J. Am. Chem. Soc.* **1986**, *108*, 3586.

(48) (a) Musher, J. I. *Angew. Chem.* **1969**, *81*, 68. (b) Schleyer, P. v. R. In *New Horizons of Quantum Chemistry*; Löwdin, P.-O., Pullman, B., Eds.; D. Reidel Publishing Co.: New York, 1983; p 95. (c) Musher, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 1370.