Articles

Specific Molecular Orbital Contributions to Nucleophilicity. The Thiocarbonyl Group as Privileged Monitor To Pinpoint Active and Less Active Molecular Orbitals in Reactions with Methylating Agents

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The rate constants for 41 compounds bearing a C=S function reacting with MeX (X = I, Tos) span 7 orders of magnitude. The PES spectra of these compounds display two very low energy peaks, which stand clearly apart from the other peaks. These two peaks correspond to the π orbitals of the C-S group; one is its CS π bonding orbital oriented out of the molecular plane (π_{CS}) and the other its p-type in-plane lone pair orbital ($\pi_{\rm S}$). For some of the compounds, the HOMO is the $\pi_{\rm CS}$ orbital and for others the HOMO is the $\pi_{\rm S}$ lone pair orbital. The best correlation (R = 0.96) between rate constants k and PES data is obtained when $\ln(k)$ is plotted against the inverse of PES energy of the $\pi_{\rm S}$ lone pair orbital. Whether this lone pair orbital is the HOMO or the next lower HOMO has no importance. A modest correlation (R = 0.78) is obtained when $\ln(k)$ is plotted against the inverse of PES energy of the $\pi_{\rm CS}$ bonding orbital. An attempt to correlate the calculated energy of the third highest occupied orbital (from AM1 calculations) with $\ln(k)$ provides a complete scattering of data (R < 0.1), but the calculated energy of the second lone pair orbital $\sigma_{\rm S}$ (≈ 90 kcal mol⁻¹ deeper than the HOMO) correlates reasonably with $\ln(k)$ (R = 0.88). The energies of the S 2s and 2p core orbitals (calculated for 13 cyclic compounds with the HF/3-21G technique to be 4000 to 5500 kcal mol⁻¹ deeper than HOMO) correlate with $\ln(k)$ (R = 0.86) as well as does that of the second lone pair orbital $\sigma_{\rm S}$. These results are the first where both frontier orbitals and core orbitals display correlation with overall reactivity. They are discussed in terms of direct (perturbational) versus indirect (nonperturbational) concepts.

The frontier molecular orbital (FMO) theory was first designed to explain the experimental selectivities reported for electrophilic substitutions of naphthalene.¹ It then became, after the Woodward-Hoffmann generalization,² a central theme pervading our understanding of thermal, as well as photochemical,³ aspects of organic,⁴ inorganic,⁵ organometallic,⁶ and biomolecular⁷ reactivity.⁸

Even with such an indisputable success, it remains somewhat of a puzzle that the complexity of a molecular

(d) Cantos, A.; Marquet, J.; Morenamanas, M.; Gonzalez-Lafont, A.;
Lluch, J. M.; Bertrand, J. J. Org. Chem. 1990, 55, 3303.
(4) (a) Fleming, I. Frontier Orbitals and Organic Chemical Reactions;
Wiley: New York, 1976. (b) Gilchrist, T. L.; Storr, R. C. Organic

assembly of electrons⁹ so often may be reduced to the simplicity of the FMO when two molecules interact to undergo a reaction. This drastic simplification has led some authors¹⁰ to question the validity of the approach, particularly with respect to which terms should vanish in a polyperturbational approach.¹¹ Rigorous testing of the model is needed.

Most of the cases studied during the last decade have concentrated on reactions where the active orbitals are all of the π out-of-plane type for a planar molecule or for

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⁸ Abstract published in Advance ACS Abstracts, March 15, 1995. (1) (a) Fukui, K. Angew. Chem., Int. Ed. Engl. **1982**, 11, 801. (b) Fukui, K.; Yonezawa, T.; Shingu, H. J. Chem. Phys. **1952**, 20, 722.

<sup>Yukui, K.; Yonezawa, T.; Shingu, H. J. Chem. Phys. 1952, 20, 722.
(2) (a) Woodward, R. B.; Hoffmann, R. Angew. Chem., Int. Ed. Engl.
1969, 8, 781. (b) Simmons, H. E.; Bunnett, J. F. Orbital Symmetry Papers; American Chemical Society: Washington, DC, 1974. (c) Woodward, R. B.; Hoffmann, R. J. Am. Chem. Soc. 1965, 87, 395.</sup>

<sup>Woodward, K. B.; Hoilmann, K. J. Am. Chem. Soc. 1965, 87, 395.
(3) (a) Fukui, K.; Tanaka, K. Bull. Chem. Soc. Jpn. 1977, 50, 1391.
(b) Reid, P. J.; Doig, S. J.; Mathies, R. A. J. Phys. Chem. 1990, 94, 8396.
(c) Nagaoka, S. I.; Nagashima, U. J. Phys. Chem. 1991, 95, 4006.
(d) Cartes A.; Marguet L.; Marguerange, M.; Corgelez Lefort A.;</sup>

^{(4) (}a) Fleming, I. Frontier Orbitals and Organic Chemical Reactions; Wiley: New York, 1976. (b) Gilchrist, T. L.; Storr, R. C. Organic Reactions and Orbital Symmetry; Cambridge University Press: London, 1979. (c) Anh, N. T. The Woodward-Hoffmann Rules; Ediscience: Paris, 1970. (d) Schipper, P. E. J. Phys. Chem. **1988**, 92, 122.

^{(5) (}a) Fukui, K.; Inagaki, S. J. Am. Chem. Soc. 1975, 97, 4445. (b)
Hoffmann, R. Angew. Chem., Int. Ed. Engl. 1982, 21, 711. (c) Stone,
F. G. A. Angew. Chem., Int. Ed. Engl. 1984, 23, 89. (d) Pearson, R. G.
Coord. Chem. Rev. 1990, 100, 403.

^{(6) (}a) Dedieu, A. Topics in Physical Organometallic Chemistry; Gielen, M., Ed.; Freund Publishing House: London, 1985; Vol. 1, p 1. (b) Tsipis, C. A. Coord. Chem. Rev. **1991**, 108, 163. (c) Weber, J.; Fluekiger, R.; Stussi, D.; Morgantini, P. Y. J. Mol. Struct. (Theochem) **1991**, 73, 175.

^{(7) (}a) Chretien, J. R.; Boudon, A.; Dubois, J. E. C.R. Acad. Sci., Paris, Ser. B 1986, 302, 1057. (b) Clayton, A. F. D.; Combs, M. M.; Henrick, K.; Mc Partlin, M.; Trotter, J. Carcinogenesis 1983, 4, 1569.
(c) Veerkamp, W.; Hutzinger, O.; Serne, P. J. Chem. Soc., Perkin Trans 2 1983, 353. (d) Adams, S. M.; Kaminsky, L. S.; Murphy, M. J. Mol. Pharmacol. 1981, 20, 423.

⁽⁸⁾ For reviews, see: (a) Herndon, W. C. Chem. Rev. 1972, 72, 157.
(b) Epiotis, N. D. J. Am. Chem. Soc. 1973, 95, 5621. (c) Houk, K. N. Acc. Chem. Res. 1975, 8, 361. (d) Eisenstein, O.; Lefour, J. M.; Anh, N. T.; Hudson, R. F. Tetrahedron 1977, 33, 523.

^{(9) (}a) Hurley, A. C. Introduction to the Electron Theory of Small Molecules; Academic Press: London, 1976. (b) Dewar, M. J. S.; Dougherty, R. C. The PMO Theory of Organic Chemistry; Plenum: New York, 1975.

^{(10) (}a) Dewar, M. J. S. J. Mol. Struct. (Theochem) 1989, 200, 301.
(b) Kahn, S. D.; Pau, C. F.; Overman, L. E.; Hehre, W. J. J. Am. Chem. Soc. 1986, 108, 7381.
(c) Bonati, L.; Moro, G.; Pitea, D.; Gatti, C. J. Mol. Struct. (Theochem) 1990, 67, 235.

a planar fragment within a molecule. We report here experimental and theoretical results for a reactive system where only in-plane lone pair molecular orbitals of π and σ types are involved in the reaction. This system is the nucleophilic reaction of thiocarbonyl compounds with MeX (X = I, Tos).

It is often stated in the literature 4,11,12 that the main factor which determines if a reaction is frontier orbital controlled or charge controlled is the magnitude of the energy gap between HOMO (nucleophile) and LUMO (electrophile). The thiocarbonyl group is especially fecund in the context of testing the FMO theory, as it presents all four possibilities of frontier/nonfrontier/ stereoactive/nonstereoactive MO's for study: (a) experimental (PES) energies are available for the HOMO and the next lower HOMO (NHOMO) of the nucleophile; (b) one of these frontier MO's is the C=S π MO (symbol = π_{C-S}), which is stereochemically inactive in thiocarbonyl reactions at carbon sp³ electrophilic centers, in analogy with carbonyl reactivity;¹³ it is often the HOMO; (c) the other frontier MO is the stereochemically active p_{π} lone pair AO on sulfur atom (symbol = π_s); it is sometimes the HOMO or the NHOMO; (d) a second stereochemically active MO is the σ lone pair on S (symbol = $\sigma_{\rm S}$); it is never a frontier MO.

Recent results from De Clercq's group provide an unexpected motive for understanding the basis for the reactivity of the C=S group, as described in this report. Indeed this group showed that compounds of the following structure are potentially active drugs against AIDS:



They inhibit quite specifically the inverse transcriptase of HIV-1 without being toxic toward the enzymes of the cell.14

Charge and Frontier Molecular Orbital Control

Frontier molecular orbital (FMO) theory derives from a perturbation expansion of the energy arising from stabilizing interactions of the filled molecular orbitals on one fragment with the empty functions on the other, and vice versa.^{1,15} Reduction of the number of expansion

(15) (a) Berson, J. A.; Salem, L. J. Am. Chem. Soc. 1972, 94, 8917. (b) Berson, J. A. Acc. Chem. Res. 1972, 5, 406.
 (16) Cavelier, F.; Pepe, G.; Verducci, J.; Siri, D.; Jacquier, R. J. Am.



Figure 1. Enthalpy of activation in reaction 2 vs logarithm of rate constant at 25 °C.

terms is the basic assumption of FMO: this assumption is that of all the terms in the perturbation equation only one needs be retained, that with the smallest denominator and corresponding to the interaction between the highest occupied MO (HOMO) of one reactant and the lowest unoccupied MO (LUMO) of the other.

One must always raise the fundamental question about the generality of the basic assumption of FMO theory that one term in the expansion is large enough to dominate the others. The combined PES and kinetic data on thiocarbonyl substrates makes it possible to specifically address this point from an experimental perspective.

Going beyond FMO, Klopman proposed¹² eq 1 to account for the energy of interaction of two molecules in solution:

$$\Delta E_{\text{total}} = -q_r q_s \frac{\Gamma}{\epsilon} + \Delta_{\text{solv}} + \sum_m^{\text{occ}} \sum_n^{\text{unocc}} \frac{2(c_r^m)^2 (c_s^n)^2 \beta_{\text{rs}}^2}{E_m^* - E_n^*} \quad (1)$$

2

The first term represents the electrostatic interaction between two atoms carrying formal charges q_r and q_s (here S of C=S and C of CH_3X). Γ is the "Coulomb repulsion term" between the two atoms r and s and ϵ is the dielectric constant of the medium. The second term represents the energy of partial desolvation of the reactants as they form the adduct. Equation 1 led Klopman to classify reactions into two types: the first is the "frontier-controlled" case, in which the dominant contribution arises from "essential" orbital interactions-the last term in eq 1; the second is the "chargecontrolled" case in which the dominant contribution arises from the electrostatic interaction of the reac $tants^{12}$ —the first term in eq 1. The AM1 calculations for our set of thiocarbonyl substrates allow us to classify their patterns of reactivity in the context of the Klopman's classification.

The logarithm of the rate constant k (ln(k)) measured for each compound of Figure 1 involved in reaction 2 will be the experimental yardstick by which the ΔE_{total} in eq 1 will be measured. As CH_3X remains the same for the

(2)
$$\begin{pmatrix} z \\ y \end{pmatrix} C = \underbrace{s:}_{CH_3} + CH_3 X \longrightarrow \begin{pmatrix} z \\ y \end{pmatrix} C = \underbrace{s:}_{CH_3} + X^-$$

whole set of studies, q_s (the charge borne by C in CH₃X),

⁽¹¹⁾ Klopman, G., Ed. Chemical Reactivity and Reaction Paths; Wiley: New York, 1974.

⁽¹²⁾ Klopman, G. J. Am. Chem. Soc. 1968, 90, 223. An analogous treatment is found in Drago, R. S. Applications of Electrostatic-Covalent Models in Chemistry; Surfside Scientific Publishers: Gainesville; 1994, p 30.

⁽¹³⁾ Purcell, F. K.; Collins, J. M. J. Am. Chem. Soc. 1970, 92, 465. (14) (a) De Clercq, E. Recherche 1992, 241, 292. (b) Baba, M. Biochem. Biophys. Res. Commun. 1989, 165, 1375. (c) Pauwels, R. Nature **1990**, 343, 470.

Chem. Soc. 1992, 114, 8885.
 (17) (a) Arbelot, M.; Guimon, C.; Gombeau, D.; Pfister-Guillouzo, G. J. Mol. Struct. 1974, 20, 487. (b) Guimon, C.; Pfister-Guillouzo, G.; Arbelot, M.; Chanon, M. Tetrahedron 1974, 30, 3831. (c) Guimon, Arbelot, M.; Pfister-Guillouzo, G. Spectrochim. Acta 1975, 31A, 985. (d) Guimon, C.; Pfister-Guillouzo, G.; Arbelot, M. Tetrahedron 1975, 31, 2769. (e) Guimon, C.; Pfister-Guillouzo, G.; Arbelot, M. J. Mol. Struct. 1976, 30, 339.

 $c_{\rm s}$ (the carbon atomic orbital coefficient for LUMO in CH₃X), and $E_{\rm m}$ (the orbital energy of the LUMO in CH₃X) remain constant. The substituent variations displayed by the compounds in Table 1 variations in $q_{\rm r}$, in $c_{\rm r}$ (the atomic orbital coefficients for S of C=S group in HOMO, next HOMO (NHOMO) and deeper molecular orbitals of the nucleophile), in $\beta_{\rm rs}$ (the resonance integral between AO $\chi_{\rm r}$ and $\chi_{\rm s}$) and in $E_{\rm n}$ (the molecular orbital energies of HOMO, NHOMO, and deeper molecular orbital sof the nucleophile).

Results and Discussion

Experiments To Check that the Variations of **Rate Constants Determined for Reaction 2 May Be Applied to Eq 1.** To be able to compare rate constant variations measured in solution and the predictions of eq 1 one must first check that the set of experimental data satisfy certain conditions. First, as shown in Figures 1 2, the rate variations must not be entropy controlled; although there are variations of ΔS^* in the series, there is no consistent trend suggesting an entropy control of the reactivity. The ΔS^{\dagger} , ΔH^{\dagger} , and ΔG^{\dagger} values obtained by conductometric measurements are gathered in Table 2., the ordering of rate constants must be independent of the solvent in which reaction 2 was performed (i.e., neither ϵ nor $\Delta_{\text{solvation}}$ in eq 1 is controlling). We have found a linear correlation between the logarithms of rate constants at 25 °C measured in acetone and the logarithms of rate constants measured in acetonitrile for a limited set of compounds (1, 2, 4, 6, 9, 17, 18, 24, 25, 27, 29, 32, 34, 35, and 40).

The equation of the correlation is

$$\ln(k_{\text{MeCN}}) = 0.9 \ln(k_{\text{acetone}}) - 0.34$$
 (R > 0.99) (3)

Analogously, a linear correlation is obtained when logarithms of rate constants in acetone are plotted against logarithms of rate constants in methanol. The equation of these correlations is

$$\ln(k_{\text{MeOH}}) = 0.7 \ln(k_{\text{acetone}}) - 2.9$$
 (R > 0.99) (4)

Third, there must be no instance of inversion in the order of nucleophilic power of the substrates, as measured by the rates of reaction with MeX, when X is changed from I to Tos. The linear correlation obtained between the rate constants measured respectively with methyl iodide and methyl tosylate as alkylating agents (eq 5) guarantees this condition:

$$\ln(k_{\rm MeTos}) = 0.9 \ln(k_{\rm MeI}) - 4.7$$
 (R > 0.99) (5)

Abboud¹⁸ et al. have measured the gas-phase basicity of a wide variety of thiocarbonyl compounds by means of Fourier transform ion cyclotron resonance spectrometry (FTICR). Their substituent trends for the increase in gas-phase basicity is exactly the same as the ones reported in this work for the nucleophilicities:

Photoelectron Spectroscopic Properties of the Set of Thiocarbonyl Compounds. The thiocarbonyl



Figure 2. Entropy of activation of reaction 2 vs logarithm of rate constant at 25 $^{\circ}$ C.



Figure 3. Photoelectron spectrum of *N*-methylthiazoline-2-thione.

group, present in all the species of Table 1, possesses two properties which make it a desirable subject for a study of the FMO approach to nucleophilicity. Pfister et al. studied in depth the photoelectron spectroscopic properties of a large series of thiocarbonyl compounds.¹⁷ The first property relevant to the present study is the clear separation of the two lowest energy peaks of the spectrum from others (Figure 3). Second may introduce and These two peaks correspond to the HOMO and NHOMO; they stand in a very clean part of the spectrum and their position may therefore be measured with a good precision.

The second property is that substituent effects and molecular orbital calculations leave no ambiguity about the nature of these two molecular orbitals: one (called $\pi_{\rm S}$) lies in the molecular plane and is mainly localized (>90%) on the sulfur atom of the thiocarbonyl group; the other is of π symmetry and of high localization on the sulfur atom of the thiocarbonyl group, there being a variable participation of the out-of-plane π orbitals of the heterocyclic part.¹⁷

The data gathered in Tables 3 and 4 illustrate a third important pattern of orbital properties for our sample of substrates. For unsaturated substrates the HOMO is the C=S π -bond orbital (π_{C-S} , out-of-plane), whereas for the saturated counterparts the HOMO is in-plane p lone pair of sulfur π_{S} (compounds 31-33 and 36-41). This substituent dependence arises from the raising of the original π out-of-plane MO through its interaction with a lower

⁽¹⁸⁾ Mó, O.; De Paz, J. L. G.; Yáñez, M.; Esseffar, M.; Bouab, W.; Ballesteros, E.; Herreros, M.; Homan, H.; Lopez-Mardomingo, C.; Notario, R.; Abboud, J.-L. M. J. Am. Chem. Soc., in press.



1	CH ₃ CH ₃ C=S	15	N-N-C+3 S-C=S	30	S-S C:S
2	CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃	16 P CH	$\begin{array}{c} \mathbf{H} \\ $	31	CH_{3} CH_{3} CH_{2} CH_{2}
3	CH ₃ CH ₃ C=S Ph CH ₃	17 CH ₃ 18	$ \begin{array}{c} N-N \\ = C \\ C \\ S \\ N-N \\ - C \\ C \\ S \\ S$	32	CH_{3} CH_{3} CH_{5} $C:S$
4	CH ₃ CH ₃ C=S	19	S-S CH ₃	33	∑s>c·s
5	CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃	20 C	S-S H ₃ C-S CH ₃	34	N-N
6	CH ₃ CH ₃ CH ₃ CH ₃	21 I	S-S-C+S S-S	35	CH ₃ CH ₃
7	Pb C=S	22 [S	CH ₃	36	(CH ₃) ₂ N (CH ₃) ₂ N
8	CH ₃ CH ₃ C:S	23	S=N C=S	37	(CH ₃) ₂ N C:S CH ₃
9	CH ₃ CH ₃	CH ₃ C 24	H ₃ N-NCH ₃	38	(CH ₃) ₂ N C:S CH ₃ S
10	Ph S C:S	25	$\dot{N} = C^{CH_3}$	39	CH ₃ S CH ₃ S
11	Ph S C S	26	N=C _{CH3} CH3 NCH3 C·S	40	CH ₃ S CH ₃ O
12	CH ₃ N-N CH ₃ CH ₃ CH ₃	27	CH ₃ NCH ₃ SC:S	41	CH ₃ O CH ₃ O
13	Ph CH ₃ CH ₃ CH ₃	28	NCH ₃ 0 ^{C:S}		
14	CH ₃ CH ₃ CH ₃ CH ₃ CH ₃	29	S S S S S		

Table 2.	Rate Constants (k, 25 °	°C) and ΔH^{\dagger} , ΔS^{\dagger} , and ΔG^{\dagger}	* Measured by (Conductimetry for	Reaction 2 Involving
		Substrates 1–4	1 (Figure 1) ^a		_

			Bui v 1/	
code	$k (L \text{ mol}^{-1} \text{ s}^{-1})$	ΔG^{\ddagger} (kcal mol ⁻¹)	ΔH^{\ddagger} (kcal mol ⁻¹)	ΔS^{\ddagger} (cal mol ⁻¹ K ⁻¹)
	(1) Reaction	s in Acetone with Methyl Io	dide (X = I in Reaction 2)	
1	3.3×10^{-3}	20.8	11.9 ± 0.3	-30.0 ± 1.2
2	$1.2 imes10^{-2}$	20.1	10.7^{b}	-31.9^{b}
3	$2.1 imes10^{-3}$	21.0	13.9^{b}	-23.6^{b}
4	$1.6 imes 10^{-4}$	22.6	14.1 ± 0.3	-28.5 ± 1.2
5	$4.4 imes 10^{-4}$	22.0	13.6 ± 0.3	-28.6 ± 1.7
6	$2.7 imes 10^{-4}$	22.3	13.6 ± 0.3	-29.2 ± 1.0
7	1.3×10^{-4}	22.8	с	
8	1.4×10^{-4}	22.7	14.5 ± 0.2	-27.6 ± 0.5
, 9	5.0×10^{-5}	23.3		
10	6.5×10^{-6}	24.5	158 ± 0.6	-29.6 ± 2.0
11	7.8×10^{-6}	24.0	15.5 ± 0.0	23.0 ± 2.0
10	7.8×10^{-4}	44.4	100105	91 5 1 1 5
12	3.0×10^{-4}	22.2	12.6 ± 0.5	-51.5 ± 1.5
13	1.8×10^{-5}	22.0	13.5 ± 0.5	-30.5 ± 1.5
14	1.7×10^{-5}	24.0	14.5 ± 0.5	-31.6 ± 1.5
15	1.0×10^{-5}	24.3	15.1 ± 0.5	-30.5 ± 1.5
16	$3.5 imes 10^{-6}$	24.9	15.8 ± 0.5	-30.7 ± 1.5
17	$4.5 imes 10^{-1}$	17.9	11.7 ± 0.9	-20.6 ± 5.0
18	3.1×10^{-1}	18.1	11.3 ± 0.2	-23.1 ± 0.7
19	$2.6 imes10^{-5}$	23.7	с	
20	$3.1 imes10^{-5}$	23.6	c	
21	$2.8 imes10^{-5}$	23.6	15.3 ± 0.3	-27.9 ± 1.2
22	2.6×10^{-5}	23.7	15.9 ± 0.3	-26.2 ± 1.2
23	6.6×10^{-4}	21.8	13.6 ± 0.3	-27.2 + 1.5
24	2.6×10^{-2}	19.6	11.3 ± 0.4	-27.8 ± 2.0
25	1.6×10^{-2}	19.9	11.3 ± 0.2	-28.9 ± 0.8
20	1.0×10^{-4}	10.0	11.0 ± 0.2 14.9 ± 0.9	-29.6 ± 1.9
20	1.4×10^{-5}	22.1	14.2 ± 0.3 15.7 + 0.6	-20.0 ± 1.2
27	1.8×10^{-6}	23.9	15.7 ± 0.6	-28.7 ± 1.5
28	4.0×10^{-6}	24.8	15.6 ± 0.5	-30.7 ± 1.5
29	1.0×10^{-6}	25.7	17.9 ± 1.2	-26.1 ± 4.0
30	2.3×10^{-6}	25.1	С	
31	$3.3 imes 10^{-4}$	22.2	14.3 ± 0.3	-26.2 ± 1.2
32	1.1×10^{-4}	22.8	14.8 ± 0.8	-27.2 ± 4.0
33	$2.5 imes10^{-6}$	25.1	с	
34	$1.8 imes 10^{-1}$	18.4	11.7 ± 0.2	-22.7 ± 0.6
35	$1.7 imes10^{-1}$	18.5	11.7 ± 0.1	-22.7 ± 0.6
36	$1.6 imes10^{-3}$	21.3	12.8^{b}	-28.3^{b}
37	$4.7 imes10^{-4}$	22.0	с	
38	1.1×10^{-5}	24.2	c	
39	$4.7 \times 10^{}$	26.1	c	
40	$(7.0 \pm 4) \times 10^{-8}$	27.2 ± 0.4	d	
41	9.0×10^{-9}	28.4	P	
_	(II) Reactions	in Acetonitrile with Methyl	Iodide ($X = I$ in Reaction 2)	
1	3.6×10^{-3}	20.8	с	
2	1.4×10^{-2}	20.0	С	
4	2.8×10^{-4}	22.3	С	
6	$5.8 imes10^{-4}$	21.9	с	
9	$7.3 imes10^{-5}$	23.1	с	
17	$3.0 imes 10^{-1}$	18.2	12.1 ± 0.6	-20.2 ± 1.4
18	$2.3 imes10^{-1}$	18.3	11.5 ± 0.4	-22.8 ± 1.3
24	$2.2 imes10^{-2}$	19.7	12.5 ± 0.2	-24.1 ± 0.8
25	$1.8 imes10^{-2}$	19.8	12.1 ± 0.2	-26.0 ± 0.6
27	$4.4 imes10^{-5}$	23.4	С	
29	$3.5 imes10^{-6}$	24.9	С	
32	$1.4 imes10^{-4}$	22.7	c	
34	$1.5 imes 10^{-1}$	18.6	12.3 ± 0.1	-21.1 ± 0.4
35	1.3×10^{-1}	18.7	12.4 ± 0.5	-21.1 ± 0.6
40	$(1.2 \pm 0.3) imes 10^{-7}$	26.9 ± 0.2	c	
0	(111) Reaction $(2.5 \pm 0.2) \times 10^{-3}$	s in Methanol with Methyl	Iodide ($\mathbf{X} = 1$ in Reaction 2)	
4	$(2.0 \pm 0.0) \times 10^{-4}$	21.0 ± 0.1	I c	
32	$(1.0 \pm 0.3) \times 10^{-4}$	22.9 ± 0.1	T _c	
36	7.4×10^{-4}	21.7	t	
	(IV) Reactions	in Acetone with Methyl Tos	sylate $(X = Tos in Reaction 2)$	
1	$4.3 imes10^{-5}$	23.4	с	
2	$1.2 imes10^{-4}$	22.8	с	
3	$3.2 imes10^{-5}$	23.6	с	
4	$2.5 imes10^{-6}$	25.1	с	
5	$6.9 imes10^{-6}$	24.5	c	
6	$4.4 imes10^{-6}$	24.8	c	
7	$2.5 imes10^{-6}$	25.1	\overline{c}	
8	$2.6 imes10^{-6}$	25.1	c	

Table 2 (Continued)

code	$k \; (L \; mol^{-1} \; s^{-1})$	ΔG^{\ddagger} (kcal mol ⁻¹)	ΔH^{\ddagger} (kcal mol ⁻¹)	$\Delta S^{\ddagger} (cal \ mol^{-1} \ K^{-1})$
	(IV) Reaction	ns in Acetone with Methyl Tos	ylate $(X = Tos in Reaction 2)$	
27	$3.6 imes10^{-7}$	26.2	с	
36	$2.7 imes10^{-5}$	23.7	с	
38	$(2 \pm 0.6) imes 10^{-7}$	26.6 ± 0.2	d	

^a Rate constants are reproductible with an error of $\pm 5\%$. ΔG^{\ddagger} is obtained from Eyring's equations: $\log (k/T) = \log (\kappa k_B/h) + \Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT$ and $\Delta G^{\ddagger} = RT (\log k_B/hT - \log k/T)$. ΔS^{\ddagger} and ΔH^{\ddagger} , when given, are obtained from the measurement of rate constants at five different temperatures covering a range of 20 deg. The uncertainties given on these enthalpies and entropies of activation are statistically estimated with a P value of 0.95. ^a Not enough measurements to make a statistical evaluation or error. ^c Less than three measurements at different temperatures. ^d Measured at 25 °C only. The value, however is the average of three determinations. ^e This value is more uncertaint than the other ones because the reaction is very slow. ^f One measurement only in methanol. In this solvent, MeI slowly decomposes. For compounds 2 and 32, the given errors correspond to the experimental reproductibility (three determinations).

Table 3. Energies (Absolute Values in eV) of the Highest
Occupied Molecular Orbitals (A-B-C-D in Figure 6)
Associated with the Thiocarbonyl Group and Charge (q_S)
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code	Aª	Ba	\mathbf{C}^{b}	\mathbf{D}^{c}	$q \mathrm{s}^d$
1	(7.27) 8.09	(7.78) 8.29	10.87	12.02	-0.34
2	(7.04) 7.93	(7.68) 8.16	10.33	11.87	-0.35
3	(7.09) 8.02	(7.71) 8.26	9.74	11.95	-0.33
4	(7.68) 8.34	(8.02) 8.46	10.71	12.13	-0.24
5	(7.45) 8.30	(7.94) 8.37	10.44	12.03	-0.25
6	(7.55) 8.20	(7.98) 8.45	10.52	12.08	-0.24
7	(7.50) 8.31	(8.00) 8.46	9.91	12.10	-0.24
8	(7.54) 8.40	(8.03) 8.45	10.67	12.20	-0.26
9	(7.60) 8.50	(8.15) 8.57	9.91	12.29	-0.24
10	(8.26) 8.60	(8.49) 8.69	10.49	12.56	-0.08
11	(7.78) 8.45	(8.15) 8.65	9.80	12.50	-0.09
12	(7.63) 8.32	(8.03) 8.38	10.92	12.04	-0.31
13	(7.59) 8.31	(8.01) 8.41	9.93	$(12.05)^{e}$	-0.30
14	(7.97) 8.63	(8.15) 8.63	10.93	12.46	-0.20
15	(7.87) 8.58	(8.16) 8.64	11.38	$(12.52)^{e}$	-0.20
16	(8.04) 8.78	(8.45) 8.82	10.09	12.47	-0.21
17	(7.55) 7.70	(7.55) 7.86	10.75	11.53	-0.34
18	(7.60) 7.65	(7.60) 7.85	10.44	11.49	-0.34
19	(8.42) 8.65	(8.42) 8.82	11.18	$(12.38)^{e}$	-0.08
20	8.52	8.72	10.59	$(12.23)^{e}$	-0.09
21	(8.11) 8.58	(8.11) 8.75	9.85	$(12.23)^{e}$	-0.09
22	(8.15) 8.52	(8.15) 8.70	11.23	$(12.28)^{e}$	-0.08
23	8.31	8.34	11.22	11.83	-0.25
24	8.21	8.27	10.85	11.91	-0.29
25	8.10	8.24	10.51	11.76	-0.30
26	(7.46) 8.05	(7.98) 8.47	9.45	12.18	-0.30
27	(7.81) 8.33	(8.16) 8.59	9.44	12.33	-0.22
28	(7.94) 8.62	(8.30) 8.75	10.02	12.52	-0.21
29	(8.14) 8.56	8.72	10.00	$(12.63)^{e}$	-0.09
30	(8.10) 8.53	(8.33) 8.83	10.02	$(12.47)^{e}$	-0.08
31	(7.99) 8.59	(7.95) 8.17	9.59	11.81	-0.27
32	(8.23) 8.75	(8.04) 8.39	9.56	11.97	-0.21
33	(8.87) 9.07	(8.40) 8.69	9.18	$(12.41)^{e}$	-0.05
34	(7.25) 7.99	(7.59) 7.79	10.83	11.65	-0.36
35	(7.02) 7.97	(7.46) 7.69	10.53	11.61	-0.37
36	(8.09) 8.27	(7.82) 7.71	9.46	11.65	-0.40
37	(8.41) 8.81	(8.00) 8.10	11.55	f	-0.34
38	(8.23) 8.72	(8.01) 8.16	9.50	ť	-0.35
39	(8.97) 9.10	(8.50) 8.68	9.21	t	-0.21
40	(9.00) 9.29	(8.71) 8.73	10.82	f	-0.21
41	(9.52) 9.94	(8.99) 8.87	12.00	t	-0.33

^a For the A and B MO's the first values in parentheses correspond to the experimental determination (PES); the second values correspond to the calculated ones (AM1). A is the highest occupied $\pi_{C=S}$ -type MO and B is the highest lone pair π_S (Figure 6). ^b C is the second highest $\pi_{C=S}$ -type MO and is associated with the α,β neighborhood of the thiocarbonyl group (Figure 6); MO's associated with substituents are not given. ^c D is the σ_S lone pair (Figure 6). ^d Values calculated by AM1 use the geometries described in Table 5. ^e For these compounds more than one molecular orbital can be connected with the D type. ^f For these compounds it is not possible to associate one value with the D type.

lying substituent π MO; in the process the π out-of-plane MO loses much of its CS π -bonding character to become more or less nonbonding.



Figure 4. Correlation between $\ln(k_{25^{\circ}C})$ (reaction 2) and experimental (PES) inverse of energy E_A of the π C=S molecular orbital (A in Figure 6).

The substrates studied in this work all have both HOMO and NHOMO of π symmetry with respect to the C=S group; their energy order can be reversed and the bonding nature of one of them is variable.

Correlations between PES Properties and Nucleophilic Properties as Measured by $\ln(k)$ in Reaction 2. Figures 4 and 5 graphically display the quality of correlations obtained when the inverse of the experimental energy of π_{C-S} and that of π_S , respectively, are plotted against $\ln(k)$. That with π_S is clearly the better. That correlation (Figure 5, R = 0.96) points to the importance of the β factor in the last term of eq 1. This factor is clearly more critical than the value $E_m - E_n$: indeed even when the HOMO is of out-of-plane symmetry (π_{C-S}) it is still the lone pair π_S in-plane molecular orbital (NHOMO) which governs the correlations. The best correlation is consistent with previous modeling of transition states.^{13,19}

Comparative Participation of the Various Molecular Orbitals in Tailoring the Nucleophilicity of C=S. Various Reasons for Cancellation of Terms in Eq 1. The preceding paragraph has noted the expected critical importance of electron localization in eq 1. This importance may be simply represented in terms of orbital overlapping in the transition state.

As for carbonyl,¹³ Gombeau's results¹⁹ show that when the electrophile approaches in the plane defined by the

^{(19) (}a) Gombeau, D.; Pfister-Guillouzo, G. Can. J. Chem. 1976, 54, 118. (b) Gombeau, D.; Pfister-Guillouzo, G. Tetrahedron 1976, 54, 118.

Table 4. Contributions^a of Atoms 1-6 (See Table 5 Conventions) in Molecular Orbitals A-D (Figure 6)

			А (л	c_s)					В	$(\pi_{\rm S})$					С	(π)					D	$(\sigma_{\rm S})$		
1	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
1		0.3	0.3	0.3	0.3	0.8						1	0.5		0.5	0.5		0.5	0.3					0.9
2		0.3	0.3	0.3	0.3	0.8						1	0.5		0.5	0.5		0.5	0.3					0.9
3		0.3	0.3	0.3	0.3	0.7						1		0.6	0.2	0.2	0.7		0.2					0.8
4		0.3	0.3	0.3	0.5	0.7						0.9		0.6	0.2	0.2	0.7		0.4					0.8
5		0.3	0.3	0.3	0.5	0.7						0.9		0.6			0.7		0.2					0.8
6		0.3	0.3	0.3	0.5	0.7					0.2	0.9		0.6	0.3		0.7		0.2					0.8
7		0.3	0.3	0.3	0.5	0.7						0.9		0.6	0.3		0.7		0.2					0.8
8		0.4	0.4	0.3	0.2	0.7						1	0.4		0.5	0.5		0.5	0.3					0.9
9		0.4	0.3	0.3	0.2	0.8						1	0.5	~ ~	0.5	0.5		0.5	0.2					0.8
10		0.4	0.3	0.3	0.4	0.6		0.2			0.2	0.9		0.7			0.7		0.3					0.9
11		0.4	0.3	0.3	0.4	0.6		0.2			0.2	0.9		0.5		~ -	0.2	0.2	0.4		0 4			0.8
12		0.4	0.2	0.3	0.3	0.8						1	0.3	0.5		0.5	0.4	0.3	0.3		0.4			0.8
13		0.4	0.3	0.3	0.3	0.8					0.0	1		0.5		0.4	0.4		0.3		0.4			0.6
14		0.3	0.2	0.3	0.5	0.7					0.2	0.9		0.5		0.4	0.0		0.2		0.2			0.8
10		0.4	0.2	0.3	0.4	0.7						0.9	04	0.0	0.0	0.3	0.0	C 0.96	0.2		0.2			0.0
17		0.4	0.2	0.5	0.2	0.7						1	0.4	0.4	0.2	0.4	0.5	0.3*	0.0					0.0
10		0.4	0.4		0.3	0.7						1	0.5	0.5	0.2	0.0	0.3	0.5	0.0					0.9
10		0.4	0.4		0.0	0.8						1		0.5	0.4	0.0	0.5		0.0	0.4	0.3			0.5
20		0.5	0.5		0.0	0.0		0.2				10		0.0	0.4	0.4	0.5		0.0	0.4	0.5			0.7
21		0.5	0.5		0.0	0.0		0.2				0.9	02	0.0	06	0.0	0.0	0.30	0.0	0.0	0.0			0.5
22		0.5	0.0		0.0	0.0		0.2				0.9	0.2	0.5	0.0	0.2	0.4	0.0	0.0	0.3	0.5			0.0
23		0.3	0.5		0.3	0.0		0.2				1	0.2	0.3	0.5	0.0	0.5	0.5	0.0	0.0	0.3			0.0
24		0.4	0.4		0.4	0.7						î	0.3	04	0.5	02	0.5	0.3	0.1	04	0.0	0.3		0.8
25		0.3	0.4		0.4	0.7						ī	0.3	0.4	0.5	0.3	0.5	0.3		0.4		0.4		0.7
26		0.3	0.3	0.3	0.3	0.7						1	0.4		0.4	0.4	010	0.5^d	0.3			0.1		0.9
27		0.3	0.2	0.3	0.5	0.7						0.9	0.3		0.4	0.4		0.4^d	0.4	0.3				0.8
28		0.4	0.3	0.3	0.2	0.7						1	0.4		0.3	0.4		0.5^d	0.2					0.9
29		0.4	0.2	0.2	0.4	0.7		0.2			0.2	0.9	0.3		0.4	0.4		0.4^d	0.3	0.3			0.3	0.6^{b}
30		0.5	0.6			0.5		0.2				0.9		0.5		0.4	0.4	d	0.3			0.2	0.2	0.6^{b}
31		0.3			0.3	0.8						1		0.6			0.6		0.3					0.9
32		0.3			0.6	0.8						1		0.6			0.6	0.2	0.3				0.3	0.8
33		0.4			0.4	0.7		0.2			0.2	0.9		0.7			0.7		0.2	0.3	0.2	0.2	0.3	0.7^{b}
34		0.3	0.3		0.4	0.8						1	0.4	0.4	0.5		0.5	0.3	0.3					0.9
35		0.3	0.3		0.4	0.8						1	0.4	0.4	0.5		0.5	0.3	0.3					0.9
36		0.3			0.3	0.9						1		0.6			0.6	0.2	0.3					0.8
37		0.5				0.8						1	0.4	0.5	0.3		0.3	0.3^{e}						f
38		0.3			0.5	0.8					0.4	0.9		0.5			0.7	0.2						f
39		0.4			0.5	0.7		0.2			0.2	0.9		0.7		0.7								f
40					0.7	0.6						0.9	0.3	0.5			0.5	0.5						f
41	0.3	0.3			0.3	0.9						0.9		0.5			0.5	е						f

^a The contributions of AO's centered on atoms i (i = 1-6; see conventions in Table 5) are evaluated using the formula $[\sum_k (c_k^i)^2]^{1/2}$ (k counts AO's on atom i and j designates an MO) and keeping only 1 significant figure. Only the contributions ≥ 0.2 are given. ^b For these compounds the AO associated with the sulfur thiocarbonyl lone pair (D) participate in several MO's. The recognition of D type orbitals is therefore not straightforward. ^c This MO is ranked fifth in terms of energy because two MO's of the phenyl substituent appear in this range of energies. ^d This MO is ranked fourth in terms of energy because one MO of the benzo substituent appears in this range of energy. ^e This MO is ranked fourth in terms of energy. ^f For these compounds the AO associated with the sulfur thiocarbonyl lone pair (D) participates in several MO's and the recognition of a single D-type orbital is not possible.

heterocyclic moiety and according to a direction of about 110° with respect to the C-S axis, the best overlap is expected between the $\pi_{\rm S}$ molecular orbital (B in Figure 6) and the σ^* -antibonding orbital of CH₃X.

Under these conditions, both the overlap between the π_{C-S} molecular orbital (A in Figure 6) and the σ^* -antibonding orbital of CH₃X and β are 0. Interpreted in the context of eq 1 this $\ln(k) - E\pi_{C-S}$ correlation is unexpected. Therefore, within the polyperturbational approach, the $\ln(k) - E\pi_{C-S}$ correlation is an indirect one. It arises just because the $E\pi_{C-S}$ values are correlated with the π_S values as shown in Figure 7.

The participation of the next lower molecular orbital of π symmetry (C in Table 3) to the nucleophilic reactivity is shown in Figure 8. The complete scattering may be understood by looking at the localization of this molecular orbital (Table 4 and Figure 6). Besides being of π outof-plane symmetry, this molecular orbital possesses a very low atomic orbital coefficient on the sulfur atom which suggests that in eq 1 this molecular orbital should have a negligible weight in the overall summation. The molecular orbital D (Table 3), the second "lone pair" orbital of the C=S group is of σ C-S symmetry (Figure 6) and lies about 90 kcal deeper than the frontier orbital (A). Its AM1 representation suggests a strong atomic character (Table 4) localized on the thiocarbonyl sulfur.

Within an approximate correspondence between the usual molecular orbital and the localized orbital (valence bond) descriptions of the C=S bond,²⁰ it corresponds to the second lone pair borne by the thiocarbonyl sulfur atom. Figure 9 shows that its energy, calculated by AM1 for the various members of the studied population, correlates better than MO A (Figure 4) but worse than MO B (Figure 5) with the nucleophilicity of the thiocarbonyl group.

This correlation is interesting; although the possible participation of sublying orbitals of appropriate symmetry has been theoretically hinted at,^{15a} the present set of results provides clear cut *experimental* evidence of a such possibility.

⁽²⁰⁾ Thompson, H. B. Inorg. Chem. 1968, 7, 604.



Figure 5. Correlation between $\ln(k_{25^{\circ}C})$ (reaction 2) and experimental (PES) inverse of energy $E_{\rm B}$ of the S lone pair (B in Figure 6).



Figure 6. Molecular orbital diagram of compound 17.

Going Deeper in Energy to Check for a Correlation of Nucleophilicity with Nonbonding Orbitals of Appropriate Symmetry. The correlative pattern of molecular orbital D (Figure 9) suggests that nucleophilic patterns of reactivity could be connected to other deeperlying orbitals of appropriate symmetry rather than to a single frontier molecular orbital. To check this possibility, we selected a set of 13 cyclic substrates (1, 4, 8, 10, 14, 17, 19, 24, 29, and 31–34) and performed ab initio calculations (HF/3-21 G)²¹ to study the correlative pattern of core atomic orbitals. Figures 10 and 11 show that a qualitative trend indeed emerges.

The most highly nucleophilic substrates are indeed the ones for which the energies associated with 2s and 2p orbitals are highest. In analogy with the $\pi_{C=S}$ molecular orbital examined in the preceding paragraphs, the cor-



Figure 7. Correlation between experimental (PES) energies of E_A (π C=S) and E_B (π S) molecular orbitals (A and B MO's in Figure 6).



Figure 8. Plot of $ln(k_{25^{\circ}C})$ (reaction 2) versus calculated (AM1) inverse energy E_C of molecular orbital C (Figure 6).

relation here is also indirect since $\beta^2/E_{mn} \approx 0$. Core ionization energies have sometimes been correlated with the ability of a molecule to accept charge at a particular location.²² The present results are the first ones where frontier orbitals and core orbitals both correlate with the same type of reactivity.

Is the Thiocarbonyl Group a Typical Frontier Controlled Nucleophile? Edwards clearly demonstrated that the ranking according to nucleophilic power of a set of compounds may be totally upset when the reference electrophile is changed.²³ A typical example

^{(21) (}a) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Memius, L. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohleing, L. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, D. J.; Pople, J. A. *Gaussian 86*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984. (b) Binkley, J. S.; Pople, J. A.; Hehre, W. J. J. Am. Chem. Soc. 1980, 102, 939. (c) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. J. Am. Chem. Soc. 1982, 104, 2797. (d) Pietro, W. J.; Francl, M. M.; Here, W. J.; De Frees, D. J.; Pople, J. A.; Binkley, J. S. J. Am. Chem. Soc. 1982, 104, 3039.

^{(22) (}a) Beach, D. B.; Eyermann, C. J.; Smit, S. P.; Xiang, S. F.; Jolly,
W. L. J. Am. Chem. Soc. 1984, 106, 536. (b) Thomas, T. D.; Siggel, M.
R. F.; Saethre, L. J. J. Electron Spectrosc. Relat. Phenom. 1990, 51, 417. (c) Nordfors, D.; Martensson, N.; Agreen, H. J. Electron Spec. Relat. Phenom. 1990, 51, 129.

^{(23) (}a) Edwards, J. O. J. Am. Chem. Soc. **1956**, 78, 1819. (b) Davies, R. E. J. Am. Chem. Soc. **1969**, 91, 1. (c) For graphical representations of these inversions of nucleophilic rankings see refs 23d and 23e. (d) Purcell, K. F.; Kotz, J. C. Inorganic Chemistry; Saunders: Philadelphia, 1977; p 224. (e) Arbelot, M.; Chanon, M. Tetrahedron Comput. Methods **1990**, 3, 307.



Figure 9. Correlation between $\ln(k_{25^{\circ}C})$ (reaction 2) and calculated (AM1) inverse energy $E_{\rm D}$ of molecular orbital D (Figure 6).



Figure 10. Correlation between the calculated energy (HF/3-21 G) of the core 2p atomic orbital on S in the C=S group and the nucleophilicity of C=S for cyclic compounds.

is provided by CH₃O⁻, which displays a high reactivity toward sp³ C electrophilic centers (CH₃X) but very low reactivity toward the more highly polarizable Pt^{II} electrophilic center (Ptpy₂Cl₂). In reacting with this Pt^{II} electrophilic center, thiourea displays a far higher nucleophilicity ($n_{pt}^{\circ} = 7.17$) than CH₃O⁻ ($n_{pt}^{\circ} < 2.4$).²⁴ The best nucleophile Et₃P toward Pt^{II} has a n_{pt}° value of 8.85.

This result classifies the thiocarbonyl nucleophile as a group prone to react as a typical frontier controlled reagent. The correlation equations in Figures 4, 5, and 6-11 confirm this conclusion.

Pearson proposed another method to measure the polarizability of a nucleophile: this method is based on the ratio r of reaction rates of the nucleophile toward methyl iodide and methyl tosylate, respectively.²⁵ For our set of thiocarbonyls this ratio is 90 and it is to be



Figure 11. Correlation between the calculated energy (HF/ 3-21 G) of the core 2s atomic orbital on S in the C=S group and the nucleophilicity of C=S for cyclic compounds.



Figure 12. Role of the charge 9s (AM1) borne by the sulfur atom in thiocarbonyl group for its nucleophilicity $(\ln(k_{25^{\circ}C})$ in reaction 2).

compared with those found for the nucleophiles of highest polarizability on this scale: $Pd(PEt_3)_3$, 3×10^5 ; $Ni(PEt_3)_4$, 8×10^5 ; $CpW(CO)_3^-$, 1.5×10^5 .

This comparison suggests that the nucleophilic reactivity of the thiocarbonyl group may not be completely governed by the third term of eq 1. Indeed Figures 12 and 13 (with R = 0.58) show that the charge borne by the sulfur atom of the thiocarbonyl group does not play a strong role in the overall nucleophilicity. The first (ionic) term of eq 1 has a small influence on the reactivity.

An unexpected outcome of Figure 12 originates from one cluster of points situated in the lower right corner. The compounds giving rise to this cluster are more reactive than the AM1 calculated global charge would suggest. The heterocyclic ring compounds forming this cluster all have sulfur atoms in addition to the one associated with the thiocarbonyl group. One reason why these compounds stand somewhat apart could be a specific treatment of the sulfur atom in the AM1 approach. Figure 13 shows that an ab initio treatment of

⁽²⁴⁾ Tobe, M. L. Inorganic Reaction Mechanisms; Nelson T. and Sons: Sunbury-on-Thames, 1976; p 51.
(25) Pearson, R. G.; Figdore, P. E. J. Am. Chem. Soc. 1980, 102,

⁽²⁵⁾ Pearson, R. G.; Figdore, P. E. J. Am. Chem. Soc. 1980, 102, 1541.



Figure 13. Role of the charge qS (HF/3-21 G) borne by the sulfur atom in the thiocarbonyl group of cyclic compounds for its nucleophilicity $(\ln(k_{25^{\circ}C})$ in reaction 2).

the thiocarbonyl compounds leads to the same overall trend. It would seem therefore as if the sulfur atoms present in the heterocyclic moiety were boosting the nucleophilicity of the thiocarbonyl group in a way somewhat reminiscent of the α effect.²⁶ Curiously, this specific behavior of compounds 10, 11, 19–22, 29, 30, and 33 is present in the correlation involving the first term of eq 1 but not in the third one. Several features of the α -effect are still poorly understood;²⁷ it is generally thought to be unimportant for substitution at a saturated carbon²⁸ although some counterclaims are known.²⁹

Conclusion

To our knowledge, this is the first set of results which examines the correlative behavior of several molecular orbitals centered at a reactive atom, in a large population of related nucleophiles, with the rate constants measuring the nucleophilicity of that atom. For example, Abboud recently reviewed one century of physical organic chemistry around the Menshutkin reaction:³⁰ out of the 624 cited references none discusses the nucleophilic behavior from the point of view described in this report. The same holds true for the data discussed in the most recent book on the SN2 reaction³¹ and in recent theoretical overviews of bimolecular substitutions.³² In terms of the polyperturbational approach one reaches the conclusion that even for a highly polarizable nucleophile, core orbital energies may be correlated with rate constants. This conclusion is not predicted by eq 1 because the $\beta/\Delta E_{mn}$ term should make the contribution of core electrons to ΔE_{total} vanishingly small. If the polyperturbational approach is correct in this situation, then the fact that core orbital energies may be correlated with an experimental set of data is due to an independent correlation of core orbital energies with the energies of valence orbitals (indirect correlation). Such a type of correlation was reported in a study of valence shell and core ionization potentials for a series of seven alkyl iodides. This study established that the chemical shifts are probably due to variations in the electron distribution along the carbon iodine bond.³⁴ Similarly in the present study, the same structural effects which lead to energy shifts at the valence shell level could well lead to variations in the electron distribution along the carbonsulfur bond. Several previous reports correlate core orbital energies with various aspects of reactivity.^{22,33} Some controversy accompanies the physical interpretation of these correlations.³⁵ Our results suggest that while valence and core electron energies both may correlate with a given experimental measure of molecular reactivity, there is not necessarily a common physical relationship behind both correlations. The interaction of two orbitals due to their overlap may be termed in energetic terms. The first order energy of the orbital interaction is proportional to the square of the resonance integral and inversely proportional to the energy difference between the interacting orbitals. In the present case the simultaneous consideration of this general law and the observed various correlations make it possible to recognize which correlations are the more meaningful.

Computational Details

Ab initio calculations were carried out using the Gaussian 86 system of $programs^{21a}$ at the SCF-HF level, using the standard 3-21G split valence orbitals.^{21b-d}

 AMI^{36} calculations were carried out with $AMPAC^{37}$ package of programs.

The geometries of the 41 compounds (Table 1) were optimized using molecular mechanics program GEN-MOL;¹⁶ Table 5 contains the relevant geometrical data for the structural environments of the thiocarbonyl group. For HOMO and the NHOMO energies, the linear correlation between experimental (PES) values and AM1 results ($R \approx 0.9$) is comparable with these obtained by Dewar³⁶ for a set of 51 species. We have checked that AM1 and HF/3-21G provide consistent sets of data for the MO energies (R > 0.95). Abboud's theoretical calculations on the thiocarbonyl group reach the same conclusion.¹⁸ Contributions of carbon and sulfur thiocarbonyl atoms and neighborhood atoms in A, B, C, D molecular orbitals (Figure 6) are gathered in Table 4.

Experimental Section

The rate constants were determined by conductimetry using homemade equipment following the lines described by Shed-

^{(26) (}a) Grekov, A. P.; Veselov, V. Ya. Russ. Chem. Rev. 1978, 47,
(31. (b) Fina, N. J.; Edwards, J. O. Int. J. Chem. Kinet. 1973, 5, 1. (c)
Hoz, S.; Buncel, E. Isr. J. Chem. 1985, 26, 213. (d) Oae, S.; Kadoma,
Y. Can. J. Chem. 1986, 64, 1184. (e) Herschlag, D.; Jencks, W. P. J.
Am. Chem. Soc. 1990, 112, 1951. (f) Wolfe, S.; Mitchell, D. J.; Schlegel,
B.; Minot, C.; Eisenstein, O. Tetrahedron Lett. 1982, 23, 615. (g) Kice,
J. L.; Legan, E. J. Am. Chem. Soc. 1973, 95, 3912.

⁽²⁷⁾ March, J. Advanced Organic Chemistry; Wiley Interscience: New York, 1992; p 352.

^{(28) (}a) Gregory, M. J.; Bruice, T. C. J. Am. Chem. Soc. 1967, 89, 4400. (b) Oae, S.; Kadoma, Y.; Yano, S. Bull. Chem. Soc. Jpn. 1969, 42, 1110.

^{(29) (}a) Beale, J. H. J. Org. Chem. **1972**, 37, 3871. (b) Buncel, E.; Wilson, H.; Chuaqui, C. J. Am. Chem. Soc. **1982**, 104, 4896.

⁽³⁰⁾ Abboud, J.-L. M.; Notario, R.; Bertrán, J.; Solà, M. Prog. Phys. Org. Chem. **1993**, 19, 1.

⁽³¹⁾ Shaik, S. S.; Schlegel, H. B.; Wolfe, S. Theoretical Aspects of Physical Organic Chemistry: The SN2 Mechanism; J. Wiley and Sons, Inc.: New York, 1992.

 ^{(32) (}a) Vetter, R.; Zulicke, L. J. Am. Chem. Soc. 1990, 112, 5136.
 (b) Wladkowski, B. D.; Lim, K. F.; Allen, W. D.; Brauman, J. L. J. Am. Chem. Soc. 1992, 114, 9136.

 ^{(33) (}a) Siggel, M. R.; Thomas, T. D. J. Am. Chem. Soc. 1986, 108, 4360.
 (b) Siggel, M. R.; Streitwieser, A., Jr.; Thomas, T. D. J. Am. Chem. Soc. 1988, 110, 8022.

⁽³⁴⁾ Hasmall, J. A.; Mills, B. E.; Shirley, D. A.; Streitwieser, A. J. Am. Chem. Soc. 1972, 94, 4445. (35) (a) Perrin, C. L. J. Am. Chem. Soc. 1991, 113, 2865. (b) Exner,

^{(35) (}a) Perrin, C. L. J. Am. Chem. Soc. 1991, 113, 2865. (b) Exner,
O. J. Org. Chem. 1988, 53, 1810.
(36) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P.

⁽³⁶⁾ Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P.
J. Am. Chem. Soc. 1985, 107, 3902.
(37) Liotard, D. A.; Healy, E. F.; Ruiz, J. M.; Dewar, J. S. A General

⁽³⁷⁾ Liotard, D. A.; Healy, E. F.; Ruiz, J. M.; Dewar, J. S. A General Molecular Orbital Package; University of Texas at Austin: Austin, 1989.

Table 5. Geometries in the Neighborhood of Thiocarbonyl Group from GenMol¹⁶ Calculations⁴

	d_{12}^b	d_{23}	d_{34}	d_{45}	d_{51}	d_{16}	$a_{123}{}^{c}$	a ₂₃₄	a_{345}	a_{451}	a_{512}	a_{516}
1	1.42	1.42	1.36	1.42	1.42	1.68	10 9 .5	108.5	108.5	109.5	104	127.9
2	1.42	1.43	1.35	1.43	1.42	1.68	109.5	108.2	108.2	109.5	104.5	127.6
3	1.42	1.42	1.36	1.43	1.42	1.68	109.2	108.8	108.4	109	104.6	127.7
4	1.42	1.42	1.33	1.73	1.73	1.68	113.1	110.3	116.3	90	110.4	123.7
5	1.42	1.43	1.34	1.73	1.72	1.68	113	109.9	115.7	90.4	110.4	123.3
6	1.43	1.42	1.33	1.71	1.73	1.69	111.9	112.6	114.2	91.4	110	125.3
7	1.42	1.42	1.33	1.73	1.73	1.68	113.1	110.5	116	90	110.4	123.8
8	1.41	1.42	1.34	1.37	1.36	1.68	106.9	101. 9	118.9	100.5	111.8	123.2
9	1.42	1.41	1.33	1.37	1.37	1.68	107.2	100.7	120.8	99.1	112.1	122.6
10	1.74	1.73	1.32	1.73	1.74	1.68	93.5	118.5	118.5	93.5	116.1	122
11	1.73	1.73	1.34	1.73	1.73	1.68	97.1	116.2	116.6	97.1	112.7	123.9
12	1.42	1.26	1.27	1.42	1.42	1.68	110.3	113.7	107.3	106.4	102.2	128.8
13	1.42	1.26	1.27	1.42	1.42	1.68	110.4	113.4	107.7	106	102.5	128.6
14	1.42	1.27	1.26	1.73	1.72	1.68	113.2	117.7	112	89.2	107.9	124.7
15	1.42	1.26	1.26	1.73	1.72	1.68	113.4	117.3	112.5	88.8	108	125
16	1.41	1.25	1.26	1.37	1.36	1.68	107.2	108.1	116.7	98.3	109.7	124.2
17	1.42	1.27	1.42	1.33	1.47	1.68	108.8	110.1	110.1	109.9	104.8	125.8
18	1.42	1.27	1.42	1.33	1.47	1.68	108.9	110.2	109.6	105.2	105.8	126.6
19	1.73	2.0	1.73	1.34	1.48	1.68	95.8	95.8	118.9	114.1	115.3	123.2
20	1.72	2	1.73	1.35	1.48	1.68	95.1	97.3	117.3	114.2	116.1	123.5
21	1.73	2.01	1.73	1.34	1.48	1.68	95.8	96.2	118.1	115	114.9	122.6
22	1.73	2	1.73	1.34	1.48	1.68	96.1	95.7	119.4	113.2	115.6	122.9
23	1.43	1.78	1.72	1.33	1.48	1.68	109.4	91.7	114.8	112.3	11.8	123.5
24	1.42	1.42	1.42	1.42	1.47	1.68	110.1	106.7	110.3	106.4	106.5	125.9
25	1.42	1.42	1.42	1.43	1.48	1.68	110	107	110.1	106.1	106.8	126.3
26	1.42	1.33	1.40	1.33	1.42	1.68	109.6	108.4	108.4	109.6	104	128
27	1.43	1.33	1.40	1.72	1.73	1.68	114.3	110.7	114.9	88.6	111.5	123.5
28	1.42	1.32	1.40	1.36	1.36	1.68	109.2	103.4	115.5	101.7	110.3	124.2
29	1.74	1.73	1.40	1.73	1.74	1.68	96.3	116.3	116.4	96.2	114.9	122.6
30	1.73	2.02	1.73	1.40	1.49	1.68	96.1	97.4	116.8	113.9	115.6	119.8
31	1.42	1.45	1.53	1.45	1.42	1.68	106.1	104.6	104.6	106	112	123.9
32	1.42	1.47	1.53	1.81	1.72	1.68	110.3	113	107.5	92.9	116.3	121.5
33	1.72	1.81	1.5	1.81	1.69	1.67	96.4	105. 9	105	97.3	113.6	121.2
34	1.42	1.42	1.42	1.42	1.47	1.68	110.1	106.7	110.3	106.4	106.5	125.9
35	1.42	1.42	1.42	1.43	1.48	1.68	110	107	110.1	106.1	106.8	126.4
36	1.35	1.48	3.07	1.48	1.35	1.70	126	78.1	78.1	126	131.8	114.1
37	1.34	1.49	-	-	1.50	1.69	124.1	-	-	-	124.5	117.9
38	1.32	1.47	4.62	1.82	1.74	1.69	120	57.3	12.9	101.9	117.5	121.4
39	1.72	1.81	4.33	1.79	1.74	1.71	107.9	73.2	9.1	101.5	99.4	133.6
40	1.74	1.82	4.14	1.41	1.36	1.69	102.2	70.6	8.3	116.4	115.2	124.3
41	1.36	1.41	4.71	1.41	1.36	1.69	116.7	30.4	30.4	116.6	113.7	123.1

^{*a*} Examples of numbering:



The same logic of atom numbering is adopted for all the compounds in Table 1, i.e. the carbon linked to the thiocarbonyl sulfur 6 is numbered 1 and the numerotation in the five-membered ring then follows counterclockwise. These six atoms are almost in plane. Only the dihedral angle between aromatic substituent and the thiocarbonyl plane is given in degrees for molecules 3, 7, 9, 11, 13, 15, 16, 21-23: DA3 = 162, DA7 = 95, DA9 = 69, DA11 = 28, DA13 = 16, DA15 = 0, DA16 = 1, DA21 = 24, DA22 = 92, DA23 = 17. To simplify and also because the bond length variations are unimportant, we have omitted the geometries of the other atoms. ^b Lengths d_{ij} (Angströms) between atom *i* and atom *j*, corrected to two decimal places. ^c a_{ijk} angles are associated with i_j , *k* atoms (the vertex of angle i_j , *k* atom is *j*) and the values are rounded to 0.1 degree. Refer to the values for 32 in the following structure:



lowski.³⁸ Alternating current (1000-3000 Hz) was used to avoid polarization phenomena. The used cell shown in Figure 14 was adapted from the one described by Nasielski.³⁹ It consists of a main vessel of about 8 cm³ in which lie the two

electrodes. A secondary vessel of equal volume is connected to the main one. In the main vessel one introduces the solution of nucleophile in 5 cm³ of solvent and, in the secondary one, the methylating reagent (in 5 cm³ of solution). The start of

Table 6. Conductance (Ω^{-1}) of Solutions of Methylthio-ylium Iodide Salt of Compound 4 in Acetone

			t	emperature (°C	()		
$concentration \ (mole \ L^{-1})$	15.5	19.9	21.9	24.95	29.95	35.1	39.9
9.8530 E-05	4.76 E-05	4.92 E-05	5.02 E-05	$5.15 ext{ E-05}$	5.34 E-05	5.51 E-05	5.62 E-05
6.5687 E-05	3.41 E-05	$3.53 ext{ E-05}$	3.60 E-05	$3.70 ext{ E-05}$	3.81 E-05	$3.95 ext{ E-05}$	4.11 E-05
4.9765 E-05	2.65 E-05	2.78 E-05	2.85 E-05	2.93 E-05	3.07 E-05	3.20 E-05	3.28 E-05
3.8410 E-05	2.12 E-05	2.21 E-05	2.24 E-05	2.31 E-05	2.41 E-05	$2.50 ext{ E-05}$	2.60 E-05
2.4633 E-05	1.42 E-05	$1.50 ext{ E-05}$	1.54 E-05	$1.59 ext{ E-}05$	1.65 E-05	1.72 E-05	1.78 E-05
1.4075 E-05	9.10 E-06	9.42 E-06	1.04 E-05	1.07 E-05	$1.10 ext{ E-05}$	1.13 E-05	1.16 E-05
9.8530 E-06	6.82 E-06	7.00 E-06	7.57 E-06	7.73 E-06	8.06 E-06	8.38 E-06	8.67 E-06
8.2100 E-06	$5.92 ext{ E-06}$	6.12 E-06	6.35 E-06	6.48 E-06	6.73 E-06	7.03 E-06	7.23 E-06
6.1580 E-06	4.81 E-06	$5.02 ext{ E-06}$	4.60 E-06	4.73 E-06	4.89 E-06	5.07 E-06	5.23 E-06
4.9265 E-06	4.12 E-06	4.28 E-06	4.09 E-06	$4.25 ext{ E-06}$	$4.38 ext{ E-06}$	$4.56 ext{ E-06}$	4.70 E-06



Figure 14. Conductimetric cell used for kinetic measurements.

the reaction is effected by a gentle swing which mixes the contents of the main vessel with that of the secondary one.

The calibration measurements made it possible to associate a concentration of salt (product in reaction 2) with the conductivity of a solution at a given temperature. The actual kinetic set of data corresponded to the very start of the reaction (first 5% of conversion at most) and only small concentrations of salt were formed. In this range of concentrations and in the range of explored temperatures a quasilinear relation between conductance of solution and salt concentration holds. A set of calibration measurements in acetone for methyl(3methyl-3H-thiazol-2-ylidene)sulfonium iodide is gathered together in Table 6. These results are graphically displayed in Figure 15. The results of linear correlations of the kind

$$z = \alpha_{t,s} \, c + \beta_{t,s}$$

where z is the conductance (Ω^{-1}) , c is the concentration (mol $l^{-1})$, $\alpha_{t,s}$ is the slope associated to a set of determinations performed in the solvent s at the temperature t, and $\beta_{t,s}$ is the value of z for c = 0 under the same conditions are collected in Table 7.

$$c = \alpha'_{t,s} \, z + \beta'_{t,s} \tag{6}$$

with $\alpha'_{ts} = 1/\alpha_{ts}$ and $\beta'_{ts} = \beta_{ts}/\alpha_{ts}$. The values of the correlation coefficients ($r^2 > 0.99$; Table 7) established that the linear model is satisfactory for the domain where it has been used.

Our determinations on a large population of compounds^{40,42,43} have shown that on the range of temperature 10–35 °C a linear relation between $\alpha_{t,s}$ (eq 6) and temperature *t* holds. Similarly, a linear correlation between $\beta_{t,s}$ (eq 6) and *t* is observed. Figures 16 and 17 illustrate these correlations for the selected example.

A large number of calibrations established that the average value of $\alpha_{t,s}$, at a given temperature, does not vary much with the structural changes in the salt studied in this work. The most differing values of $\alpha_{t,s}$ at the same temperature in the same solvent do not differ by more than 5%.

The order of reaction is controlled by the proportionality between the initial concentration in reagent and the initial rate of reaction. This proportionality was checked for most of the reactions in acetone. Furthermore the kinetic measurements never pass a conversion greater than 5%; these conditions favor a simple bimolecular mechanistic scheme because the secondary reactions seldom have begun to interfere in this range of conversions. Supplementary experiments were performed to check that no chain mechanism involving electron transfer was participating in the overall conversion. For compounds **10**, **17**, and **19** the addition of 10% of trinitrobenzene to the solution led to almost no change for the rate constant. For compounds **1** and **4** the reaction was followed by ESR and no radical appeared during the reaction.

Rate constants are extracted from experiments using the classical differential equation $dx/dt = k_T(a_o - x)(b_o - x)$ with dx/dt being the rate of formation of the salt, x the concentration of salt at the time t, a_o and b_o the initial concentrations of reactants, and k_T the rate constant at the temperature T. The integration gives two solutions:

$$\ln((a_{o} - x)/(b_{o} - x)) = (a_{o} - b_{o})k_{T}t + \ln(a_{o}/b_{o})$$
(7)

$$\mathbf{x}/(a_{0} - \mathbf{x}) = a_{0}k_{T}t \tag{8}$$

Equation 7 is the general case $(a_o \neq b_o)$. Plotting $y = \ln((a_o - x))(b_o - x))$ vs *t*, a linear correlation is obtained whose the slope is k_T . Calibrations provide a direct connection between the measured conductance and *x*. Thus,

$$y = (a_{o} - b_{o})^{-1} \ln [b_{o}(a_{o} - \alpha'_{t,s}/R + \beta'_{t,s})/a_{o}(b_{o} - \alpha'_{t,s}/R + \beta'_{t,s})]$$
(9)

Every rate constant was obtained by a classical least-square treatment of the plot conductivity versus time from 20 or more experimental points. Figure 18 illustrates this calculation for the reaction between 4 and CH_3I in acetone at five temperatures.

It has been repeatedly checked that this method provides constants in full agreement with completely independent

⁽³⁸⁾ Shedlowsky, T. *Physical Methods*; Weissberger, A., Ed., Interscience Publishers: New York, 1960; Vol. 4.

⁽³⁹⁾ Coppens, G.; Declerck, F.; Nasielski, J. Bull. Soc. Chim. Belg. 1963, 72, 25.

^{(40) (}a) Gallo, R.; Chanon, M.; Lund, H.; Metzger, J. *Tetrahedron Lett.* **1972**, 3857. (b) Cottet, R.; Gallo, R.; Metzger, J. *Bull. Soc. Chim. Fr.* **1967**, 4499. (c) Berg, U.; Gallo, R.; Metzger, J.; Chanon, M. *J. Am. Chem. Soc.* **1976**, *41*, 2621.

⁽⁴¹⁾ Brown, H. C. J. Chem. Educ. 1959, 36, 424.

⁽⁴²⁾ Arbelot, M.; Gallo, R.; Chanon, M.; Metzger, J. *Phosphorus Sulfur* **1976**, *1*, 271.

⁽⁴³⁾ Arbelot, M. Thesis, Université d'Aix-Marseille III, Marseille, 1980.



Figure 15. Example of conductance cell calibration: (+) 15.50, (◊) 19.90, (○) 21.90, (△) 24.95, (×) 29.95, (●) 35.10, (▲) 39.90 °C.



Figure 16. $\alpha = 3.71$ E-03 t + 0.415 r² = 0.99.



Figure 17. $\beta = 3.33$ E-08 t + 1.86E-06 r² = 0.99.

determinations from the literature.^{40,41} The ΔG^{\ddagger} , ΔH^{\ddagger} , and ΔS^{\ddagger} values are the result of rate constant determinations at five temperatures spread on an interval of 20 °C. Larger temperature intervals are difficult to obtain for the present study because on the low-temperature side crystallization of the salts

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Table 7. Linear Correlation between Conductances and Concentrations from Table 6 and Figure 15

<i>t</i> (°C)	$\alpha_{t,s} \ (eq \ 6)$	$\beta_{t,s}$ (eq (6) r^2
15.5	4.71 E-01	2.35 E-0	06 0.998
19.9	4.88 E-01	2.50 E-0	06 0.997
21.9	$4.97 ext{ E-01}$	2.63 E-0	0.997
24.95	$5.10 ext{ E-01}$	2.73 E-0	0.996
29.95	5.29 E-01	2.85 E-0	06 0.996
35.1	5.47 E-01	3.01 E-0	06 0.996
39.9	5.60 E-01	3.19 E-0	06 0.994
0.08			
€ 5 0.06 5 0.06 0.04 0.02 0.02 0.00			ARA ARA ARA ARA
	. 0 50 .	<u>8</u> 8	
		ten	nps (s)
			1
у д	= 7.223E-05x +	8.116E-06	□ 288.66 °K
y♦	= 1.068E-04x +	2.996E-05	• 293.06 °K
уo	= 1.635E-04x +	5.043E-05	• 298.11 °K
у ▲	= 2.468E-04x +	6.789E-05	▲ 303.11 °K
у∎	= 3.690E-04x +	1.865E-04	■ 308.26 °K
	$r^2 > 0.99$	98	

Figure 18.

interferes and, on the high-temperature side, volatility of MeI has to be taken care of.

All compounds studied in this work are known. Their structures were confirmed by NMR, IR, and MS. Purity was assessed by TLC.

The studied products were either prepared in our laboratory (1, 4-6, 8, 10, 12, 17, 18, 21, 22, 24-28, 31-33, 35, and 36) or graciously gifted by Professor Sandström (2, 3, 7, 9, 12-16), Dr. Pfister-Guillouzo (11, 19, 20, 30, 37-41), Professor Le Coustumer (23), or Professor Guglielmetti (29).

The purification techniques for these materials are as follows: [compound number (recrystallization media)^{reference}] 1 (benzene),⁴² 2, 3 (ethanol),⁴⁴ 4 (ethanol),⁴⁵ 5 (tolueneheptane),⁴⁴ 6 (ethanol),⁴⁵ 7-9 (toluene-heptane),⁴⁴ 10 (hexane),⁴⁶ 11 (hexane),⁴³ 12 (1-propanol),⁴⁷ 13 (ethanol),⁴⁷ 14 (light petroleum),⁴⁷ 15, 16 (ethanol),⁴⁷ 17, 18 (chloroform-diethyl ether),⁴⁸ 19 (ethanol),⁴³ 20 (ethanol),⁴⁹ 21 (cyclohexane),⁵⁰ 22 (cyclohexane),⁵¹ 23 (column chromatography; silica gelpetroleum ether), 43,52 24, 25 (ethyl acetate), 53 26 (benzene), 54

- (47) Sanström, J.; Wernerbeck, I. Acta Chem. Scand. 1966, 20, 57.

- (4) Sanström, J.; wernerbeck, I. Acta Chem. Schul. 1966, 20, 51.
 (48) Begtrup, M. J. Chem. Soc., Perkin Trans. 1 1975, 507.
 (49) Trebault, C.; Teste, J. Bull. Soc. Chim. Fr. 1966, 3790.
 (50) Thuillier, A.; Vialle, J. Bull. Soc. Chim. Fr. 1959, 1398; 2182.
 (51) Teste, J.; Lozac'h, N. Bull. Soc. Chim. Fr. 1953, 561.
 (52) Lecoustumer, G.; Mollier, Y. Bull. Soc. Chim. Fr. 1970, 3076.
 (53) Kroger, C. F.; Sattler, W.; Beyer, H. Ann. Chem. 1961, 643, 121.
- (54) Fukati, K. J. Pharm. Soc. Jpn. 1954, 74, 1365.

⁽⁴⁴⁾ Kjellin, G.; Sandström, J. Acta Chem. Scand. 1969, 23, 2879. (45) Roussel, C.; Babadjamian, A.; Chanon, M.; Metzger, J. Bull. Soc. Chim. Fr. 1971, 1902.

⁽⁴⁶⁾ Chen, C. H. J. Chem. Soc., Chem. Commun. 1976, 950.

Specific MO Contributions to Nucleophilicity

27 (methanol-water),^{55,43} 28 (benzene),⁴² 29 (chloroformethanol),⁵⁶ 30 (ethanol),⁵⁷ 31 (ethanol),⁴³ 32 (benzene-cyclohexane),⁵⁸ **33** (ethanol),⁴³ **34**, **35** (ethyl acetate),⁵⁹ **36** (hexane),⁴³ 37-41 (column chromatography; silica gel-petroleum ether).⁴³

The salts used for the conductivity cell calibration were prepared by reaction of methyl iodide on the thiocarbonyl compound in a sealed tube and were washed with anhydrous

diethyl ether. They were recrystallized as follows: Methylthioylium iodide compounds from 1, 12, 13, 16, 26, 31 (methanol), 43 4, 27 (ethanol),⁴³ 23 (ethanol),⁵² 10, 14, 21, 22, 32 (vacuum-dried in the presence of P_2O_5).⁴³

The solvents and methyl iodide used for kinetic measurements were twice distilled just prior use.

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^{(55) (}a) Chambonnet, A. Thesis, Marseille, 1962. (b) Halasa, A. F.;

 ⁽b) (a) (b) (a) Hüenig, S.; Fleckenstein, E. Liebigs Ann. Chem. 1970, 738, 192.
 (b) Appriou, P. Thesis, Brest 1977.

⁽⁵⁷⁾ Legrand, M.; Mollier, Y.; Lozac'h, N. Bull. Soc. Chim. Fr. 1953, 327.

⁽⁵⁸⁾ Bafford, R. A.; Chanon, F.; Chanon, M.; Metzger, J. Bull. Soc. Chim. Fr. 1973, 3, 971.

⁽⁵⁹⁾ Begtrup, M. Acta Chem. Scand. 1975, B29, 141.