

partial separation of the product mixture. Elution of **2a** as an oil overlapped with that of **1a** and **7a** which is formed by rearrangement of **2a**. The identity of **7a** was confirmed by independent synthesis. Hydroxylation of **3** with *m*-chloroperoxybenzoic acid in  $\text{CH}_2\text{Cl}_2$  at  $0^\circ$  yielded 2,4-dimethoxy-6-methylphenol (**8**),<sup>16</sup> which was converted to **7a**,<sup>14</sup> mp 56–57°.

The ir spectrum (neat) of **2a**<sup>17</sup> displayed bands at 2830 ( $\text{CH}_3\text{O}$ ), 1740 ( $\text{C}=\text{C}$ ), and 1615  $\text{cm}^{-1}$  ( $\text{C}=\text{C}$ ); the uv spectrum (hexane)  $\lambda_{\text{max}}$  316 nm ( $\log \epsilon \sim 2.6$ ); and the pmr spectrum (100 MHz,  $\text{CDCl}_3$ ) a singlet at  $\delta$  2.01 (3 H,  $\text{OCOCH}_3$ ), a triplet at  $\delta$  5.58 for  $\text{H}_e$ ,  $J_{ee} = 2.0$  and  $J_{de} = 2.5$  Hz, a triplet at  $\delta$  5.16 for  $\text{H}_c$ ,  $J_{ee} = 2.0$ ,  $J_{ac} = 2.0$ , and  $J_{cd} \sim 0$  Hz, a doublet of doublets at  $\delta$  5.07 for  $\text{H}_d$ ,  $J_{de} = 2.5$  and  $J_{ad} = 1.4$  Hz, a doublet at  $\delta$  4.65 for  $\text{H}_b$ ,  $J_{ab} = 1.4$  Hz, a singlet at  $\delta$  3.62 (3 H,  $\text{CH}_3\text{O}$ ) overlapping with a multiplet for  $\text{H}_a$  at  $\delta$  3.58, and a singlet at  $\delta$  3.24 (3 H,  $\text{CH}_3\text{O}$ ). The pmr assignments were confirmed by the spectrum of **2b**, prepared by photolysis of **1b**,<sup>18</sup> in which  $\text{H}_c$  and  $\text{H}_d$  were absent and  $\text{H}_a$  and  $\text{H}_e$  appeared as doublet,  $J_{ab} = 1.4$  Hz, and singlet, respectively. All other resonances were unaltered with respect to the spectrum of **2a**. Further confirmation of the structural assignment was obtained by spin decoupling. With irradiation of  $\text{H}_a$ ,  $\text{H}_e$  was unaltered,  $\text{H}_b$  appeared as a singlet, and  $\text{H}_c$  and  $\text{H}_d$  appeared as doublets,  $J_{ee} = 2.0$  and  $J_{de} = 2.5$  Hz, respectively.

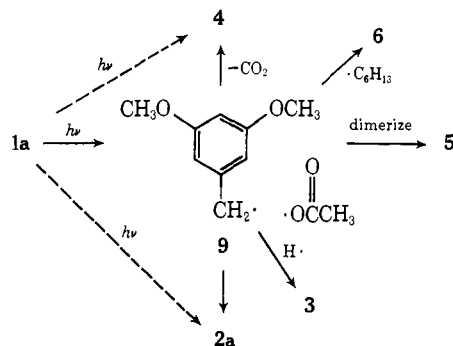
When a 0.017 *M* benzene solution of **2a**<sup>17</sup> was stirred at  $55^\circ$  for 3 hr, **2a** was converted in  $\sim 90\%$  yield to **7a**. Analogously, **2b** yielded **7b** (eq 1). The rearrangements



of **2a** and **2b** to **7a** and **7b**, respectively, support the structural assignment of **2**.<sup>20,21</sup> It is interesting to note that **2** rearranges to **7** in an apparently thermal process by a symmetry-forbidden<sup>22</sup> [1,3]-hydrogen shift and not to **1** by symmetry-allowed<sup>22</sup> [1,3]- or [3,3]-acetoxy shifts.

The formation of **3**, **4**, **5**, and **6** is consistent with initial photoinduced cleavage of **1a** to give 3,5-dimethoxybenzyl (**9**) and acetoxy free radicals, Scheme I.

Scheme I



- (16) E. Späth, M. Pailer, and G. Gregely, *Chem. Ber.*, **73**, 795 (1940).  
 (17) This material was contaminated with 7.9% **1a** and 3.4% **7a**.  
 (18) Lithium aluminum deuteride reduction of methyl 3,5-dimethoxybenzoate<sup>19</sup> yielded 3,5-dimethoxybenzyl-*l,l-d\_2* alcohol, which was converted to **1b**.  
 (19) C. Bülow and G. Riess, *Chem. Ber.*, **35**, 3900 (1902).  
 (20) The parent hydrocarbon, 5-methylene-1,3-cyclohexadiene, has been prepared; W. J. Bailey and R. A. Baylouny, *J. Org. Chem.*, **27**, 3476 (1962).  
 (21) Attempts to form a Diels-Alder adduct with dimethyl acetylenedicarboxylate and with tetracyanoethylene were unsuccessful.  
 (22) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 114–119.

Hydrogen abstraction by and dimerization of **9** yield **3** and **5**, respectively. Decarboxylation of acetoxy radical followed by combination of resultant methyl radical and **9** yields **4**, which could also result from a concerted photoinduced expulsion of  $\text{CO}_2$  from **1a**. Hydrogen abstraction from solvent by **9**, acetoxy, or methyl radical would yield hexyl radical, which combines with **9** to yield **6**. Formation of **2a** can proceed by recombination of **9** and acetoxy radical or by a concerted process from **1a**. For the latter route photochemical [1,3]- and [3,3]-acetoxy shifts are symmetry allowed and forbidden,<sup>22,23</sup> respectively. For a thermally excited ground state both shifts should be symmetry allowed.<sup>22</sup> We plan to investigate the mechanism of the **1** to **2** transformation.

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(23) A referee has suggested that use of *n* electrons on the carbonyl oxygen could allow a photochemical [3,3] process.

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### Frontier Control Nucleophilic Reactivity and Photoelectron Spectroscopy Data within the Klopman Equation. The Thiocarbonyl Group

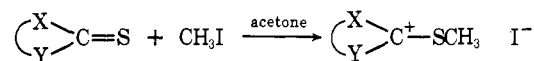
Sir:

Many equations correlating the rate of reaction between various nucleophiles and electrophiles with physicochemical parameters have been established.<sup>1–6</sup> The approach of Hudson and Klopman<sup>5,6</sup> illustrates the relative importance of the control of reactivity by charges and by frontier orbitals.

Unfortunately this approach has been difficult to check experimentally because of the lack of a tool capable of measuring the effective energies of orbitals involved in reactivity. Photoelectron spectroscopy (pes) now fills this gap.

We wish to report the results arising from a comparison of kinetic measurements<sup>7</sup> and the ionization potentials of some heterocyclic thiocarbonyl compounds.

The kinetics of the reaction have been studied by a



conductometric method previously described.<sup>8,9</sup> The

- (1) J. O. Edwards, *J. Amer. Chem. Soc.*, **76**, 1540 (1954).  
 (2) J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962).  
 (3) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3571 (1963); *Chem. Eng. News*, **43**, 90 (1965); *Chem. Brit.*, **3**, 103 (1967); *J. Chem. Educ.*, **45**, 581 (1968).  
 (4) R. S. Drago and B. B. Wayland, *J. Amer. Chem. Soc.*, **87**, 3571 (1965).  
 (5) G. Klopman and R. F. Hudson, *Theor. Chim. Acta*, **8**, 165 (1965).  
 (6) G. Klopman, *J. Amer. Chem. Soc.*, **90**, 223 (1968).  
 (7) M. Arbelot, R. Gallo, M. Chanon, and J. Metzger, *Int. J. Sulfur Chem.*, in press.  
 (8) R. Cottet, R. Gallo, J. Metzger, and J. M. Surzur, *Bull. Soc. Chim. Fr.*, **12**, 4502 (1967).  
 (9) M. Chanon, R. Gallo, J. M. Surzur, and J. Metzger, *Bull. Soc. Chim. Fr.*, **7**, 2881 (1968).

Table I. Experimental Ionization Potentials ( $I_n$ ), Experimental ( $\log k$ ), and Theoretical ( $\Delta E$ ) Reactivity

Nucleophile	Code	$I_n$ (eV) ( $\pm 0.02$ )	$-\log k$ ( $\pm 0.02$ )	$\Delta E$	Relative error (%)
1,3-Dimethylimidazoline-2-thione	1	7.78	2.50	2.40	4
3,4,5-Trimethylthiazoline-2-thione	2	7.94	3.36	3.43	2
1,3-Dimethylimidazolidine-2-thione	3	7.95	3.48	3.49	0
3,4-Dimethylthiazoline-2-thione	4	7.98	3.57	3.67	3
1,3-Dimethylbenzimidazoline-2-thione	5	7.98	3.84	3.67	4
3-Methylthiazoline-2-thione	6	8.02	3.80	3.91	3
3,4,5-Trimethyloxazoline-2-thione	7	8.03	3.85	3.96	3
3-Methylthiazolidine-2-thione	8	8.04	3.97	4.02	1
5-Phenyl-1,2-dithiol-3-thione	9	8.11	4.55	4.41	3
5-Thienyl-1,2-dithiol-3-thione	10	8.15	4.59	4.63	1
3-Methylbenzothiazoline-2-thione	11	8.16	4.77	4.68	2
3-Methylbenzoxazoline-2-thione	12	8.30	5.40	5.39	0

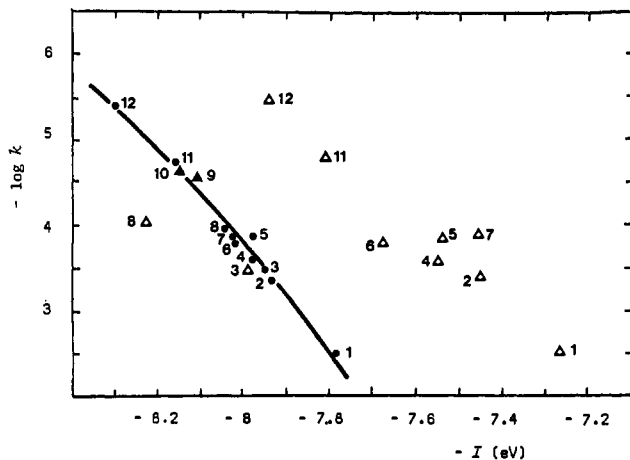


Figure 1. Key:  $k$ , rate constant for the reaction with methyl iodide in acetone at 25°;  $I$ , ionization potential determined by pes;  $\Delta$ , first  $\pi$  level;  $\bullet$ , nonbonding level;  $\blacktriangle$ , first  $\pi$  and nonbonding levels have the same values. The drawn curve corresponds to eq 2. For numerical code see Table I.

ionization potentials have been determined by photoelectron spectroscopy.<sup>10,11</sup>

Figure 1, which gives the values of experimental reactivity ( $-\log k$ ) as a function of the experimental ionization potentials  $-I_n$  and  $-I_\pi$ , clearly shows that there is a better correlation of nucleophilicity with the nonbonding  $n$  energy levels ( $-I_n$ ) than with the bonding  $\pi$  levels ( $-I_\pi$ ). These values give a good approximation to the energies associated with the corresponding molecular orbitals, from the Koopman theorem.<sup>12</sup>

The two ionization potentials of lowest energy result from the ionization of electrons from two molecular orbitals strongly localized on the sulfur atom of the thiocarbonyl group, one being a bonding orbital with  $\pi$  symmetry, the other a nonbonding orbital with  $\sigma$  symmetry.

There being no single relationship between the calculated charge<sup>13</sup> on the sulfur atom of the thiocarbonyl group and the observed reactivity, and since the two last occupied molecular orbitals are of low energy, the

(10) C. Guimon, M. Arbelot, and G. Pfister-Guillouzo, submitted for publication in *Spectrochim. Acta*.

(11) D. Gombeau, C. Guimon, J. Deschamps, and G. Pfister-Guillouzo, submitted for publication in *J. Electron. Spectrosc. Relat. Phenomena*.

(12) T. Koopman, *Physica (Utrecht)*, **1**, 104 (1934).

(13) The charge was calculated using the CNDO/S method, taking into account the effect of the  $d$  orbitals: C. Guimon, D. Gombeau, and G. Pfister-Guillouzo, *Tetrahedron*, **29**, 3399 (1973).

reaction studied seems to be a typical case of frontier orbital control as defined by Klopman<sup>6</sup> (eq 1).

$$\Delta E = \Delta \text{solv}(1) + \sum_{\text{occ}} \sum_n \frac{2(c_r^m)^2 (c_s^n)^2 \beta_{rs}^2}{E_m^* - E_n^*} \quad (1)$$

The localizations of the nonbonding molecular orbitals on the sulfur atom are of the same order ( $C_r^m(S) = 0.976 \pm 0.010$ ) for all nucleophiles considered.

Furthermore, with the electrophile ( $\text{CH}_3\text{I}$ ) and the solvent being constant and the nucleophiles being of similar nature, the differences in solvation can be considered as negligible and  $\beta_{rs}$  will be essentially the same. Thus in this particular case, Klopman's equation can be simplified to

$$\Delta E = a + [b/(E_m^* - E_n^*)]$$

where  $a$ ,  $b$ , and  $E_n^*$  are constants.

If  $E_m^*$  is compared with the energy of the nonbonding orbital ( $-I_n$ ) as determined by pes, then the anharmonic rule of hyperbolic curve is verified for all the points (Figure 1) corresponding to the nonbonding levels.

The best correlation between the theoretical ( $\Delta E$ ) and experimental ( $-\log k$ ) values is found with a value of  $E_n^*$  between  $-3$  and  $-5$  eV. For this later value which corresponds to that proposed by Klopman for a moderately hard electrophile, the equation of the curve drawn in Figure 1 is

$$\Delta E = 21.34 + [52.68/(-I_n + 5)] \quad (2)$$

The difference between the experimental points and those calculated by this relationship is within the experimental errors (Table I).

Thus the nucleophilic character of this very polarizable species is correctly described by a frontier-control method applied to the nonbonding molecular orbital associated with the lone pairs on the sulfur atom of the thiocarbonyl group.

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