value of 2.6 mM was obtained for the K_s in the oxidation of guaiacol. This reaction was inhibited noncompetitively by CN⁻ ions with a K_i value of 0.1 mM. The effect of pH on this enzyme was similar to that described for the *M. fascicularis* enzyme.

This report suggests that the human and monkey salivary lactoperoxidases have some common properties such as sensitivity to CN⁻ ions and molecular weight values. The reported values of the molecular weight of human salivary peroxidase range from 73 500 to 89 000.[9,11] Values of 80 000 to 100 000 have been reported for the molecular weight of a human saliva antibacterial factor which most likely corresponded to lactoperoxidase.[12] Other similarities between the human and monkey parotid saliva lactoperoxidases are the iso-electric points of the main molecular forms.[10] The monkey salivary lactoperoxidases clearly differed from the human salivary enzyme in their lower stability upon being subjected to molecular-permeation chromatography and other purification steps after CM-cellulose fractionation.

1. Wright, R. C. and Tramer, J. J. *Dairy Res. 25* (1968) 104.
2. Pickering, A., Oram, J. D. and Reiter, B. *J. Dairy Res. 29* (1962) 151.
3. Morrison, M. and Hultqvist, D. E. *J. Biol. Chem. 238* (1963) 2847.
4. Reiter, B. and Oram, J. D. *Nature 216* (1967) 328.
5. Morrison, M. and Allen, P. Z. *Science 152* (1966) 1626.
6. Morrison, M. and Steele, W. F. In Person, P., Ed., *Biology of the Mouth*, American Association for Advancement of Science, Washington, DC 1968, pp. 89 – 110.
7. Mäkinen, K. K., Bowen, W. H., Dalgard, D. and Fitzgerald, G. *J. Nutr. 107* (1978) 779.
8. Chance, B. and Maehly, A. H. In Colowick, S. P. and Kaplan, N. O., Eds., *Methods in Enzymology*, Academic, New York 1964, Vol. II, p. 764.
9. Mäkinen, K. K., Tenovuo, J. and Scheinin, A. *J. Dent. Res. 55* (1976) 652.
10. Mäkinen, K. K. and Tenovuo, J. *Acta Odontol. Scand. 34* (1976) 141.
11. Morrison, M., Bayse, G. and Danner, D. J. In Schultz, J., Ed., *Biochemistry of the Phagocytic Process*, North-Holland, Amsterdam 1970, pp. 51 – 56.
12. Iwamoto, Y. and Matsumura, T. *Arch. Oral Biol. 11* (1966) 667.

Received April 13, 1978.

A Note on the Methyl Inductive Effect in Sulfides

JAN A. PAPPAS

Institute of Physics, Box 1038 Blindern, University of Oslo, Oslo 3, Norway

The methyl group is usually classified as electron-donating relative to hydrogen. This is partly based on the observed effect of methyl substitution on acid and base strengths. There are, however, several experimental observations that cast doubt on these interpretations,[1] supported by molecular orbital calculations showing the methyl group to be electron-attracting (relative to hydrogen) in simple alcohols and amines.[2]

It is the purpose of this communication to show that, according to molecular orbital theory, a methyl group is *electron-attracting* also when bound to sulfur in the forms commonly occurring in organic chemistry. Furthermore, we will show that the simple correlation that usually is assumed to exist between high charge density of an anion and a corresponding high proton affinity or gas-phase base strength, does not seem to be valid.

The quantum mechanical method used was the MO-LCAO-SFC method using a double-zeta Gaussian basis including $3d$-orbitals on sulfur. Further computational details can be found elsewhere.[3] The molecular geometries used were partially optimized and partially based on previous experience in sulfur systems.[3,4]

The molecules studied were those listed in Table 1 together with the corresponding calculated proton affinities and atomic charges on sulfur. Also listed are the dipole moments of the neutral molecules as these will reflect redistribution of the electrons. The relation
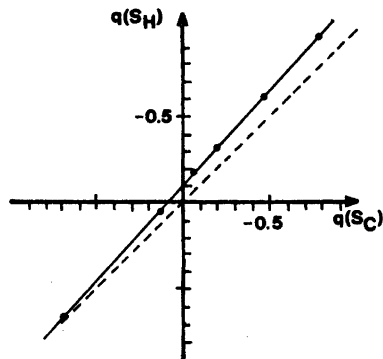

Fig. 1. The atomic charge on S bound to H, $q(S_H)$, *versus* the atomic charge on S bound to C, $q(S_C)$. The broken line represents equal charge on S_H and S_C.

Table 1. Energies and atomic populations.

Compound	Proton affinity/kcal mol^{-1}[e]		$q(S)$	Dipole moment/Debye [a]	
	Calc.	Exp.		Calc.	Exp.[b]
HS$^-$	375.8	337 [7]	−.963		
CH$_3$S$^-$	380.6		−.784		
H$_2$S$_2^-$			−.619 [4]		
(CH$_3$)$_2$S$_2$H$^-$			−.465 [4]		
H$_2$S	173.6	178[8], 195 [9]	−.323	1.34	0.974 [b]
CH$_3$SH	190.4	201 [9]	−.193	1.67	1.52 [b]
H$_2$S$_2$ [d]	175.8		−.177	1.46	1.18 [c]
(CH$_3$)$_2$S$_2$ [d]			−.057	2.14	1.45 [c]
HS$^+$			+.670		
CH$_3$S$^+$			+.688		

[a] Dipole moments of ions are not reported as they depend on the origin of the coordinate system. [b] Gas phase values. [c] Benzene as solvent. [d] From Ref. 3. [e] 1 kcal mol^{-1} = 4.184 kJ mol^{-1}.

between the atomic charges on sulfur bound to H and sulfur bound to methyl as shown in Fig. 1 and the table, clearly demonstrates that a methyl group is *electron-attracting* relative to hydrogen in this series of compounds, even when bound to sulfur atoms with moderate positive charges. This inability of a methyl group to neutralize excess positive charge implies that it cannot be considered as a structure capable of dispersing excess charge in general, although previous observations indirectly have indicated so.[6]

As both the experimental and calculated dipole moments of sulfides increase upon methylation, one might argue that this implies an increasing polarization of the compound in the sense that charge is transferred towards the negative sulfur atom. To understand this apparent inconsistency between the calculated electron transfer from the sulfur atom and the change in dipole moments, it is necessary to take into account the dipole moment of a methyl group itself (being polarized C$^{\delta-}$H$_3^{\delta+}$). When substituted in a sulfide (polarized like H$_2^{\delta+}$S$^{\delta-}$) this will add up with the dipole moment of the sulfide itself. The total dipole moment of the compound will accordingly increase even in the hypothetical case of no charge transfer between methyl and sulfur. So merely an increase of dipole moments on methylation of sulfides is not conclusive as to charge redistributions in the compound.

The proton affinities reported in the table were obtained as the differences between the total energies of the corresponding ions and neutral compounds. It is difficult to calculate proton affinities to a high accuracy, but it nevertheless appears to be a significant trend that methylation increases the proton affinities slightly both of the anions and the neutral compounds. Although very little quantitative experimental information about the energies of protonation is available for comparison, it is

gratifying that the trend in the only known case is reproduced correctly. A different trend is observed in amines and alcohols where methylation is found to increase the proton affinities of the anions and decrease those of the neutral compounds.[2] This is a reminder that great care must be exercised when looking for universal effects of methylation as they may turn out to be essentially dependent on the local environment.

The result that methylation increases the proton affinities but decreases the charge densities of the acceptor sulfur atom, suggests that the energies of proton transfer reactions do not necessarily correlate with the charge densities at the acceptor atoms. This means that acid and base strengths not necessarily may be deduced from the knowledge of the electron donating or accepting properties of the substituents.

1. Brauman, J. I. and Blair, L. K. *J. Am. Chem. Soc. 96* (1968) 6561.
2. Hehre, W. J. and Pople, J. A. *Tetrahedron Lett. 34* (1970) 2959.
3. Pappas, J. A. *J. Am. Chem. Soc. 99* (1977) 2926; *Chem. Phys. 12* (1976) 397.
4. Pappas, J. A. *J. Chem. Soc. Perkin Trans. 2* (1978). *In press.*
5. Mc Clellan, A. L. *Tables of Experimental Dipole Moments*, W. H. Freeman and Co., San Fransisco 1974.
6. Tel, L. M., Wolfe, S. and Csizmadia, I. G. *J. Chem. Phys. 59* (1973) 4047.
7. Gáspár, R., Tamassy-Lentei, I. and Kruglyak, V. *J. Chem. Phys. 36* (1962) 740.
8. Beauchamp, J. L. and Buttrill, S. E. *J. Chem. Phys. 48* (1968) 1783.
9. Hobrock, B. G. and Kiser, R. W. *J. Phys. Chem. 66* (1962) 1648.