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Calculation of Partial Charges on Functional Groups in Organic Compounds

B. S. SEKHON

Department of Chemistry
Punjab Agricultural University,
Ludhiana-141 004, India

The principle of electronegativity equalization has been applied for the calculation of group partial charge on functional groups in organic compounds. The increasing alkyl chain length increased partial negative charge on groups such as OH, COOH, $CONH_2$, COCl, $OC(O)CH_3$, OC_2H_5, NH_2, CHO and Cl. The partial negative charge on various groups decrease in the order: acid chloride > ester > amide > aldehyde > chloro > alcohol > ether > amine for each alkyl group. The reactivity of organic compounds is correlated with the partial charge on functional group.

INTRODUCTION

A significant development in the electronegativity concept has been provided by Sanderson formulation of the principle of electronegativity equalization[1,2]. The physical and chemical properties of substances are largely determined by the partial charges on the constituent atoms[3,4] and the evaluation of these partial charges is an important electronegativity application. Bratsch[5] described a method for the calculation of equalized electronegativity (X_{eq}) and the estimation of group partial charge. X_{eq} was calculated according to

$$X_{eq} = \frac{N + q}{\Sigma\left(\frac{v}{x}\right)}$$

where $N = \Sigma v$ = the number of atoms in the species formula and q is the charge of the species. The net partial charge on groups was calculated by

$$S_G = N_G\left(\frac{X_{eq} - X_G}{X_G}\right)$$

where N_G is the number of atoms in the group formula, X_G is given by

$$X_G = \frac{N_G}{\Sigma\left(\frac{v}{x}\right)}$$

The reactivity of organic compounds can be understood in terms of group partial charge on various functional groups and such an attempt has not been made so far. The partial charge on various groups in peptides[6], lipids[7] and carbohydrates[8] have been reported earlier. The present communication, therefore, deals with the calculation of group partial charge in organic molecules using equalized electronegativity values obtained by Bratsch method.[5]

RESULTS AND DISCUSSION

The values of equalized electronegativity (X_{eq}) and partial charge on some organic functional groups for alkyl groups namely CH_3, C_2H_5, C_3H_7, C_4H_9 and C_5H_{11} are summarized in Table 1. X_{eq} Values decrease with increase in alkyl chain length in each class of organic compounds. Each functional group possess partial negative charge which increase with increasing alkyl chain length. The results also showed that the partial negative charge on functional groups decrease in the order: $COCl > COOH > OCOCH_3 > CONH_2 > CHO > Cl > OH > OC_2H_5 > NH_2$ for each alkyl group.

The reactivity of organic compounds is understandable in terms of partial charge possessed by a functional group which has been calculated using X_{eq} values obtained by Bratsch method[5] (Table 1). Within the series of acid derivatives, relative reactivities towards a common nucleophile (e.g. water) generally decrease in the order[9a]:

Acid chlorides > esters > amides

The partial negative charges on these groups also decrease in the same sequence. It is thus apparent that higher is the partial negative charge on a functional group, higher is the reactivity of organic compound containing that group. The order of reactivity of the subclasses of alcohols: tertiary > secondary > primary, for nucleophilic substitution reaction of alcohols[9b] involving rupture of the C–O bond is easily explained on basis of partial positive charge on alkyl group (Table 2). The partial positive charge on alkyl group in alcohols decrease in the sequence: tertiary > secondary > primary. It is therefore indicated that greater is the partial positive charge on alkyl group, greater is its ability to attract nucleophile. Likewise the order of case of dehydration of alcohols to form alkenes is tertiary > secondary > primary and may be correlated to the partial negative charge on OH group in tertiary, secondary and primary alcohals (Table 2) which decreases in the similar sequence. Higher is the partial negative charge on OH group, greater is its affinity towards H^+ to form protonated alcohol (ROH_2^+) which is the first step in the mechanism involving dehydration of alcohols to form alkenes[9c].

Basicity of amines and ammonia is also correlated with the partial negative charge on NH_2/NH group. Higher is the partial negative charge on a group, greater is its ability to accept proton. The data (Table 2) show that the partial negative charge on NH_2 group in ammonia is less than in methylamine. Further, in methylamine NH_2 group has lesser partial

TABLE 1

EQUALIZED ELECTRONEGATIVITY (X_{eq}) AND PARTIAL CHARGE VALUES ON VARIOUS FUNCTIONAL GROUPS IN ORGANIC COMPOUNDS *X_{eq} VALUES, **PARTIAL CHARGE.

Alkyl group R	Functional group								
	OH	COOH	CHO	$CONH_2$	COCl	$OCOCH_3$	OC_2H_5	NH_2	Cl
CH_3	2.4000*	2.5130	2.4195	2.4480	2.5407	2.4525	2.3570	2.3380	2.4130
	−0.210**	−0.412	−0.248	−0.298	−0.461	−0.306	−0.127	−0.105	−0.236
C_2H_5	2.3670	2.4525	2.3840	2.4106	2.4650	2.4195	2.3420	2.3280	2.3714
	−0.236	−0.496	−0.288	−0.370	−0.537	−0.397	−0.158	−0.118	−0.250
C_3H_7	2.3510	2.4190	2.3655	2.3890	2.4265	2.3985	2.3360	2.3230	2.3530
	−0.247	−0.544	−0.309	−0.411	−0.575	−0.453	−0.180	−0.124	−0.255
C_4H_9	2.3420	2.3985	2.3540	2.3745	2.4030	2.3840	2.3216	2.3196	2.3427
	−0.254	−0.5735	−0.322	−0.439	−0.600	−0.494	−0.226	−0.130	−0.258
C_5H_{11}	2.3358	2.3840	2.3462	2.3644	2.3870	2.3735	2.3195	2.3170	2.3360
	−0.259	−0.594	−0.331	−0.458	−0.615	−0.522	−0.232	−0.132	−0.260

TABLE 2

GROUP PARTIAL CHARGES IN SUBCLASSES OF ALCOHOLS AND AMINES

Compound	Partial Charge	
	OH	Alkyl
CH_3CH_2OH	−0.2355	+0.2355
$(CH_3)_2CHOH$	−0.2475	+0.2475
$(CH_3)_3COH$	−0.2540	+0.2540
	NH_2/NH	
HNH_2	−0.074	
CH_3NH_2	−0.105	
$(CH_3)_2NH$	−0.176	

negative in magnitude than NH group in dimethylamine. The basicity constant (K_b) values for ammonia, methylamine and dimethylamine are 1.8×10^{-5}, 4.4×10^{-4} and 5.2×10^{-5} respectively[9d]. It is well known that the higher the K_b, the stronger the basicity of the amine and it is thus apparent that the aliphatic amines are stronger bases than ammonia. The present results, therefore, provide evidence that the magnitude of the partial charge on a functional group helps us in understanding the reactivity of organic compounds.

REFERENCES

1. R. T. Sanderson, *Science*, **114**, 670 (1951).
2. ———, Chemical Bonds and Bond Energy, Academic Press, New York, p. 76 (1976).
3. ———, Chemical Periodicity, Reinhold, New York, (1960).
4. ———, Inorganic Chemistry, Reinhold, New York, pp. 69, 81, (1967).
5. S. G. Bratsch, *I. Chem. Educ.*, **62**, 101 (1985).
6. B. S. Sekhon, *Sci. Cult.*, **55**, 101 (1989).
7. ———, *Natl. Acad. Sci. Letters*, **13**, 235 (1990).
8. ———, *Proc. Indian Natl. Sci. Acad.* (In press).
9. J. R. Holum, Principles of Physical, Organic and Biological Chemistry, John Wiley and Sons, Inc., New York, (a) p. 420, (b) p. 325, (c) p. 330, (d) p. 370 (1969).

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