Asian Journal of Chemistry Vol. 19, No. 7 (2007), 5161-5168

Relationship Between Coefficient and Compressibility of Carbenium Ion Hydrolysis Rate

S. NOORIZADEH
Department of Chemistry, College of Sciences, Shahid Chamran University
Ahvaz, 61357-43169, Iran
E-mail: noorizadeh_s@scu.ac.ir; noorizadeh_110@yahoo.com

A linear relationship between the rate constant of hydrolysis and a recently introduced parameter, group compressibility of a series of proposed carbenium ions (28 ions) are shown as log k_w = 17.00224–4.28332Gβ′. According to these group compressibilities, a new substituent constants, σ_p (Gβ′), are also introduced, which correctly explains the experimental electrophilicity ordering established in terms of experimental scales.

Key Words: Carbenium ion, Group compressibility, Hammett substituent constant, Hydrolysis rate.

INTRODUCTION

Carbenium ions are among the most reactive species in organic chemistry. With only a sextet of electrons on carbon these molecules are unstable, exceedingly reactive particles and therefore they can undergo a wide variety of reactions[1-3]. There is a revival of interest in the reactivity of carbocations in solution following the development of important empirical scales of nucleophilicity and electrophilicity[4,5]. The stability of these ions in solution has been studied by many authors using theoretical[6-10] and experimental techniques[11-13].

There are many global properties such as, hardness, dipole moment, electrophilicity, *etc.*, which are related to the reactivity of molecules. Two new chemical concepts have also been recently introduced in our research group, namely, the atomic compressibility and group (molecular) compressibility, which can be easily evaluated for each molecule[14]. The former is defined for an atom and has the following form:

$$\beta = \left(\frac{12\,\pi^2\varepsilon_0}{e^2}\right)\frac{r^4}{Z_{eff}} \tag{1}$$

in which r and Z_{eff} are the radius and the effective nuclear charge of the corresponding atom, respectively. The later concept, group compressibility, is calculated for molecules and is defined simply as:

$$G\beta = \sum_{i=1}^{N}\beta_i \tag{2}$$

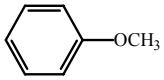
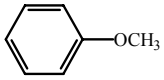
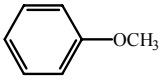
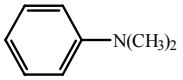
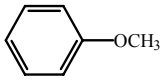
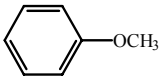
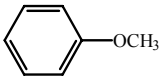
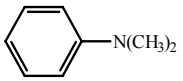
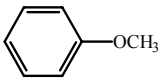
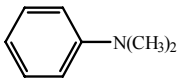
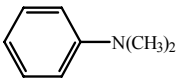
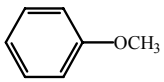
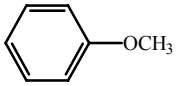
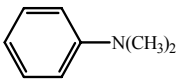
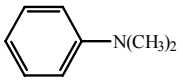
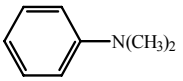
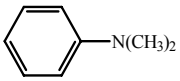
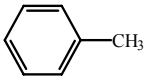
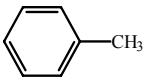
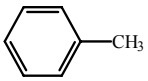
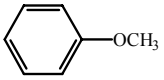
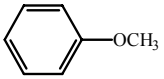
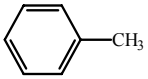
where β_i is the compressibility of the ith atom in the proposed molecule and N is the total number of atoms in the molecule. We can simplify the compressibility by factoring out a constant ($12\pi^2\varepsilon_0/e^2$) in each case and therefore the $\frac{r^4}{Z_{eff}}$ value (represented by β') can be simply calculated for each atom. This parameter calculated for 45 elements and a wide range of molecules with different functional groups[14]. The compressibilities obtained for these molecules showed a good linearity with the corresponding polarizabilities. The physical meaning of these two compressibility parameters was examined briefly in Donald work[15].

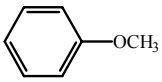
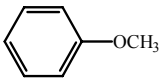
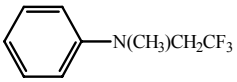
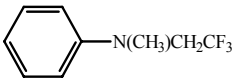
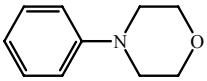
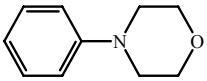
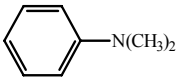
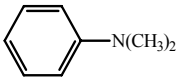
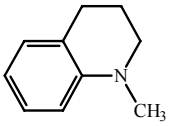
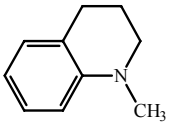
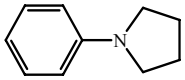
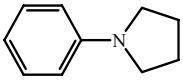
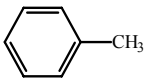
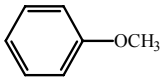
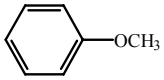
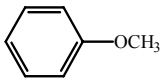
Not only for environmental exposure and risk analysis[16], but rate constants (*e.g.*, of hydrolysis) are also important to industries that try to improve speciality chemicals. Recently the local electrophilicity of a series of carbenium ions has been ranked within an absolute theoretical scale and a relationship has been found between this parameter and rate coefficients for the hydrolysis of carbenium ions[17]. They have also introduced a new substituent constant to account for the responses of the electrophilicity pattern induced by multiple substitutions at the carbocation site. Since there is an urgent need for reliable and low-cost methods for predicting rate constants of organic compounds[18], we apply the new concept (group compressibility) to estimate the values of hydrolysis rate for a variety of carbenium ions by a simple calculation. The main reason for this being the possibility of generating reliable data, obtained by a simple method when all the experimental values are not available.

RESULTS AND DISCUSSION

The selected carbenium ions in this work are presented in Table-1. These molecules can be classified in three categories: tritylium (**1-9**), benzhydrylium (**10-20**) and benzylium (**21-28**) ions. They are so arranged in this table that in each class the rate of hydrolysis decreases. As it is mentioned before, Aizman and co-workers[17] calculated the electrophilicities for these carbocations and showed there is a linear relationship between this parameter and the logarithm of hydrolysis rate constants, log k_w with the correlation coefficient equal to 0.93781. Since both of the compressibility parameters (atomic and group compressibilities) are a measure of the tendency of an atom or a molecule in changing its volume in an external electric filed, therefore we have claimed that they can also be used as reactivity descriptors in chemical reactions. We have looked for such relation between compressibility value and the log k_w for carbenium ions. The group compressibility of a carbenium ion is calculated easily by summation of the atomic compressibilities of the constituted atoms of the proposed molecule (eqn. 2). The atomic compressibilities which are used

TABLE-1
THE CONSIDERED CARBENIUM IONS IN THIS STUDY

Compd.	R_1	R_2	R_3
1			
2			
3			
4			
5			
6			
7			
8			
9			
10	H		
11	H		
12	H		
13	H		
14	H		

Compd.	R_1	R_2	R_3
15	H		
16	H		
17	H		
18	H		
19	H		
20	H		
21	H	CH_3	
22	CH_3	CH_3	
23	H	CH_3	
24	H	H	
25	H	CH_3	
26	H	OCH_3	
27	CH_3	OCH_3	
28	CH_3	OCH_3	

in these calculations are 0.061388, 0.121848, 0.084469, 0.071397 and 0.055604 for H, C, N, O and F atoms, respectively[14]. Table-2 summarizes the evaluated group compressibilities and the logarithm of the rate constants for the hydrolysis of the selected ions. For the whole set of 28 carbeniums a good linear relation is obtained between the evaluated compressibilities and the hydrolysis rate constants, which is shown in Fig. 1. Regression analysis is developed *via* the Curve Expert 1.3 software and it is observed that:

$$\log k_w = 17.00224 - 4.28332\, G\beta' \quad (3)$$

The linear dependence between both variables has high statistical significance (r = 0.95364) and is better than that of Aizman *et al.*[17]. This linearity is qualitatively acceptable if one considers that this series of ions comprises a large variety of different structures. The most deviations are seen for compounds **4** and **18**. Therefore, as it is claimed, compressibility can be further considered as a reliable descriptor of reactivity.

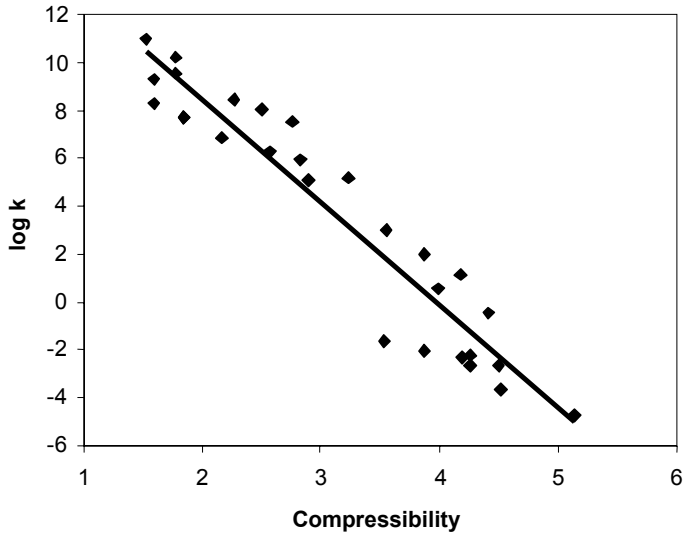


Fig. 1. Logarithm of the rate coefficients of hydrolysis *vs.* group compressibility values for the 28 selected carbenium ions

To analyze the effect of different substituents on the rate coefficients, Aizman *et al.*[17] considered those compounds that have two fixed hydrogen atoms at the *p*-position of the phenyl group, which according to Hammett classification have $\sigma_p(H) = 0.0$ and the third phenyl group substituted at *p*-position with H (compound **1**), OCH_3 (compound **2**), $N(CH_3)_2$ (compound **4**) and *p*-CH_3 (not included in this series). They showed that for this short series the σ_p increases linearly with the local electrophilicity index and

TABLE-2
LOGARITHM OF HYDROLYSIS RATE CONSTANTS, CALCULATED GROUP COMPRESSIBILITIES AND THE OBTAINED SUBSTITUENT CONSTANTS USING ELECTROPHILICITY AND COMPRESSIBILITY FOR THE SELECTED CARBOCATIONS

Compd.	m.f.	log k_w [S^{-1}][a,b]	Gβ′[Å^4]	$\sigma_p(\omega)$[c]	σ_p(Gβ′)
1	$C_{19}H_{15}$	5.18	3.235932	0.015	0.014
2	$C_{20}H_{18}O_2$	3.00	3.613341	-0.338	-0.480
3	$C_{21}H_{19}O_2$	1.98	3.867974	-0.679	-0.813
4	$C_{21}H_{20}N$	-2.02	3.871037	-0.805	-0.817
5	$C_{22}H_{21}O_3$	1.17	4.183995	-1.069	-1.227
6	$C_{22}H_{22}NO$	-2.34	4.187058	-1.044	-1.231
7	$C_{23}H_{25}N_2$	-3.68	4.506142	-1.347	-1.649
8	$C_{23}H_{24}NO_2$	-2.64	4.503079	-1.309	-1.645
9	$C_{25}H_{30}N_3$	-4.71	5.141247	-1.914	-2.480
10	$C_{13}H_{11}$	8.48	2.259292	1.137	1.293
11	$C_{14}H_{13}$	8.08	2.503916	0.822	0.973
12	$C_{15}H_{15}$	7.51	2.748540	0.557	0.653
13	$C_{14}H_{13}O$	6.32	2.575313	0.355	0.879
14	$C_{15}H_{15}O$	5.96	2.819937	0.166	0.559
15	$C_{15}H_{15}O_2$	5.11	2.891334	-0.111	0.466
16	$C_{19}H_{19}F_6N_2$	0.58[b]	3.984046	-0.805	-0.965
17	$C_{21}H_{26}N_2O_2$	-0.48[b]	4.466628	-1.132	-1.597
18	$C_{17}H_{21}N_2$	-1.59[b]	3.529502	-1.145	-0.370
19	$C_{21}H_{23}N_2$	-2.25[b]	4.139670	-1.359	-1.169
20	$C_{21}H_{25}N_2$	-2.66[b]	4.262446	-1.359	-1.329
21	C_8H_9	11.0	1.527276	2.890	2.252
22	C_9H_{11}	10.23	1.771900	2.348	1.931
23	C_9H_{11}	9.60	1.771900	1.906	1.931
24	C_8H_9O	8.30	1.598673	1.351	2.158
25	$C_9H_{11}O$	7.70	1.843297	1.087	1.838
26	C_8H_9O	9.30	1.598673	1.175	2.158
27	$C_9H_{11}O$	7.70	1.843297	0.645	1.838
28	$C_{10}H_{13}O_2$	6.85	2.159318	-0.212	1.424

a = from ref. 4,5,19; b = from ref. 20; c = from ref. 17.

therefore introduced a new substituent constant, $\sigma_p(\omega)$. These values for the whole series of carbenium ions in this work are given in the fifth column of Table-2. We do the same analysis with compressibility in order to compare our results with those of the Aizman *et al.*[17]. The group compressibility for the *p*-CH_3 tritylium ion, which is not included in the regression analysis is also calculated (3.480556 A^4). For these four compounds, which Aizman *et al.*[17] used in their analysis, a linear dependency is observed between σ_p and the corresponding compressibility values, which is shown in Fig. 2. The obtained relation is as follow:

$$\sigma_p(G\beta') = 4.25161 - 1.30938\,G\beta' \quad (4)$$

with the regression coefficient equal to 0.99751. Therefore we define a new substituent constant, $\sigma_p(G\beta')$, which is simply determined only by the knowledge of the compressibility value and does not need any rigorous and time consuming computation. The evaluated constants for the proposed carbocations are gathered in the last column of Table-2.

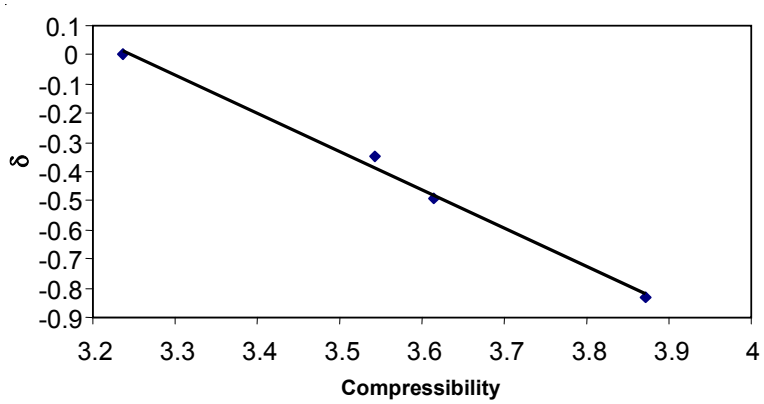


Fig. 2. Hammett substituent constants *vs.* group compressibility for singly substituted carbenium ions

For all of the selected tritylium ions (compounds **1-9**) $\sigma_p(G\beta') < 0$, which indicating that substitution at the carbocation site with *p*-OCH_3 or *p*-$N(CH_3)_2$ causes an electrophilic deactivation and these groups act as electron releasing substituents. The rate coefficients are consistently predicted to be less than the reference compound **1**. These results are similar and in accordance with the Aizman's scale.

In the benzhydrylium subseries (compounds **10-20**) both of the highest rate coefficient and activating effect is shown by the compound **10**. For all combinations of *p*-CH_3 and *p*-OCH_3 (compounds **10-15**) the global effect is activating ($\sigma_p(G\beta') > 0$), but for the other combinations in this subseries (compounds **16-20**) the effect of substitution is deactivating ($\sigma_p(G\beta') < 0$). This trend is also seen in Aizman's scale, only with one exception; compound **15**. In Aizman's model the sign of substituent constant for compound **15** is negative whereas since the compounds **14** and **15** have very similar structures, it seems that they must show the same electrophilic effect.

Finally, for the subseries of substituted benzyl ions (compounds **21-28**) we observe that the global effect is activating ($\sigma_p(G\beta') > 0$) and all of the substituent constants are more than the reference compound **1**. Again in the Aizman's model the compound **28** shows deactivating effect ($\sigma_p(\omega) <$

0), which is not reliable, because of the similarity between the structures of this compound with those of the compounds **26** and **27**, which have $\sigma_p \rangle 0$.

The only difficulty, which may seen in this method is that the isomer molecules (*e.g.*, compounds **22** and **23**), which have the same compressibility values, show the similar rate coefficients. We are working on this problem to consider the structural effect on the compressibility and i mprove the method. The compressibility is also successfully used in the kinetic study of some other reactions (such as hydrogen abstraction reactions) in our group, which will be submitted as soon as possible.

Conclusion

In this paper, a linear relation is found between the compressibilities and the logarithm of the hydrolysis rate coefficients for series of carbenium ions. According to these compressibilities, new substituent constants are also introduced to account for the responses of the electrophilic effect induced by substitutions at the carbocation site. It is concluded that compressibility parameter can be used as a reactivity descriptor in the study of chemical reactions.

REFERENCES

1. G.A. Olah, Carbocations and Electrophilic Reactions, Wiley, New York (1974).
2. H.C. Brown, The Nonclassical Ion Problem, Plenum, New York (1977).
3. P.D. Bartlett, Nonclassical Ions, W.A. Benjamin, New York (1965).
4. H. Mayr and M. Patz, *Angew. Chem., Int. Ed.*, **33**, 938 (1994).
5. H. Mayr, T. Bug, M.F. Gotta, N. Hering, B. Irrgang, B. Janker, B. Kempf, R. Loos, A.R. Offial, G. Remennikov and H. Schimmel, *J. Am. Chem. Soc.*, **123**, 9500 (2001).
6. V. Gold and B.W.V. Hawes, *J. Chem. Soc.*, 2102 (1951).
7. N.C. Deno and A. Schrisheim, *J. Am. Chem. Soc.*, **77**, 3051 (1955).
8. E.M. Arnett and R.D. Buschik, *J. Am. Chem. Soc.*, **86**, 1564 (1964).
9. H. Basch, T. Hoz and Sh. Hoz, *J. Phys. Chem.*, **103**, 6458 (1999).
10. R. Herrero, E. Quintanilla, P. Muller and J.-L. M. Abboud, *Chem. Phys. Lett.*, **420**, 493 (2006).
11. J.L.M. Abboud, O. Castano, E.W. Della, M. Herreros, P. Muller, R. Notario and J.C. Rossier, *J. Am. Chem. Soc.*, **119**, 2262 (1997).
12. J.L.M. Abboud, I. Alkorta, J.Z. Davalos, P. Muller, E. Quintanilla and J.C. Rossier, *J. Org. Chem.*, **68**, 3786 (2003).
13. J.L.M. Abboud, I. Alkorta, J.Z. Davalos, P. Muller and E. Quintanilla, *Adv. Phys. Org. Chem.*, **37**, 57 (2002).
14. S. Noorizadeh and M. Parhizgar, *J. Mol. Struct. (Theochem.)*, **725**, 23 (2005).
15. K.J. Donald, *J. Phys. Chem. A*, **110**, 2283 (2006).
16. W.J.G.M. Peijnenburg, *Pure Appl. Chem.*, **63**, 1667 (1991).
17. A. Aizman, R. Contreras and P. Perez, *Tetrahedron*, **61**, 889 (2005).
18. T.W. Collette, *Trends Anal. Chem.*, **16**, 224 (1997).
19. C.D. Ritchie, *Can. J. Chem.*, **64**, 2239 (1986).
20. S. Minegishi and H. Mayr, *J. Am. Chem. Soc.*, **126**, 5174 (2004).

(*Received*: 24 August 2006; *Accepted*: 14 June 2007) AJC-5689