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Notes

Can Internal Pressure Describe the Effect of Salt in Aqueous Diels–Alder Reactions? A Possible Explanation[†]

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Recently, a report[1] appeared that described how the rate of the Diels–Alder (D–A) reaction between *N*-ethylmaleimide and anthracene-9-carbinol in aqueous sodium salt solutions followed a linear relationship with the size of the anion of salt. Hydrophobic effects were suggested to be the major forces responsible for the increase or decrease in rate of reaction.[2a] At the end of the report, it was suggested that some surface contact between the salt and organic solute might be responsible for the hydrophobic effects and thus the increase or decrease in the reaction rates when different salts were used. In the report, other possible explanations for the effect were also not ruled out.

We were intrigued by this very suggestion, and thus, in our attempts to search for alternate explanations, we set out to investigate if the high cohesive energy of water in terms of internal pressure[3] (P_i) as altered by the salts could explain the changes in rate. We wish to point out that, although Breslow[2a] in his pioneering work had indicated the role of P_i on the kinetic profiles of the D–A reactions, he did not quantify his suggestion[2b] to explain the reaction rates in terms of P_i. In this paper, we demonstrate that internal pressure, a simple bulk property of a salt solution, can provide an alternate explanation to describe the above observations on the reaction rates.[1]

The concept of P_i provides an excellent basis for examining solution phenomena.[3] The internal pressure of a salt solution can be estimated[4] from the knowledge of isothermal compressibility, β, and thermal expansion, α, of a solution at an absolute temperature of T as $P_i = \alpha T/\beta$. For sodium salts examined in this work, except for PF_6^- and AsF_6^-, we used the literature data on the volume properties.[5] The scaled particle theory[6] (SPT) was employed to generate P_i via α and β for PF_6^- and AsF_6^- using hard core diameters.[1] In the case of guanidinium salts, i.e., GnCl and $GnClO_4$, we used surface tension data[7] to calculate α and β by the procedure described by Mayer.[8] All the calculations were performed for 2 M solutions. The calculated values of internal pressure are listed in Table I. The P_i values are accurate to ±3% as calculated from the error estimations in α and β by the SPT and experimental data,[5] wherever available.

Table I. Values of Internal Pressure, P_i, Caused by 2 M Salt Solutions

sodium salts		guanidinium salts	
salt	P_i/bar	salt	P_i/bar
Cl^-	3805	Cl^-	1445
Br^-	3740	Br^-	1420
BF_4^-	2260	BF_4^-	1246
ClO_4^-	1550	ClO_4^-	1161
PF_6^-	1460		
AsF_6^-	1391		

Let us now examine the rate constants k_2 as reported by Rizzo with respect to the internal pressure as calculated in the present work. We did not decompose the total internal pressure caused by the salt into its ionic components, as the cation is common in both sets comprising sodium and guanidinium salts. Our calculated P_i values for salts show similar trends with ionic radii of anions constituting the salts.[4] The results of k_2 versus P_i for sodium and guanidinium salts are plotted in Figure 1, where very interesting linear relationships for both types of salts–water systems are seen. The linear relationships between k_2 and P_i can be expressed as

$$k_2 = 0.11849 + 0.48788 \times 10^{-4} P_i \qquad (1)$$

for sodium salts and

$$k_2 = -8.2767 \times 10^{-2} + 1.4306 \times 10^{-4} P_i \qquad (2)$$

guanidinium salts.

We obtain standard deviations in k_2 for sodium and guanidium salts as 0.074×10^{-3} and 0.061×10^{-3} M^{-1} s^{-1}, respectively. The linear relationships indicate that internal pressure affects the rate constant in a D–A reaction in a linear fashion. The reaction rates vary with the magnitude of internal pressure, which in turn is related to anionic sizes in a set of salts with a common cation. This variation is consistent with the increasing or decreasing hydrophobic effects in the presence of these salts and their relations with the reaction rates. In addition to his explanation, we wish to point out that his results can also be easily understood using a simple bulk property of salt solution like internal pressure. If the internal pressure of a salt solution is higher, the reaction rate is higher as compared to the lower internal pressure. Since the cations are common for the sodium and guanidinium salt plots the effect of internal pressure is naturally produced by

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(1) Rizzo, C. J. *J. Org. Chem.* **1992**, *57*, 6382 and in particular ref 17 cited therein.

(2) (a) Breslow, R. *Acc. Chem. Res.* **1991**, *24*, 159 and references cited therein. For the work done in this area, see ref 1 and its references. (b) The concept of internal pressure was later discredited in the case of 5 M $LiClO_4$ in diethyl ether (a nonaqueous solution); see: Forman, M. A.; Dailey, W. P. *J. Am. Chem. Soc.* **1991**, *113*, 2761 and references cited therein.

(3) For details see: Dack, M. R. J. *Chem. Soc. Rev.* **1975**, *4*, 211 and references cited therein.

(4) Another method, however, a bit cumbersome, to calculate P_i involves the use of the Tammann–Tait–Gibson (TTG) model, which also requires the knowledge of volume properties; see: Leyendekkers, J. V. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 357 and references cited therein.

(5) (a) Sohonel, O.; Novotny, P. *Densities of Aqueous Solution in Inorganic Substances*; Elsevier: Amsterdam, 1985; 335 pp. (b) *International Critical Tables*; McGraw-Hill: New York, 1928; Vol. 3. (c) *Handbook of Chemistry and Physics*, 61st ed.; CRC Press: Boca Raton, 1980.

(6) (a) Pierotti, R. *Chem. Rev.* **1976**, *76*, 717 and references cited therein. (b) Lebowitz, J. L.; Helfand, E.; Praestgaard, E. *J. Chem. Phys.* **1965**, *43*, 774 (c) Kumar, A. *J. Am. Chem. Soc.* **1993**, *115*, 9243. Here the SPT is applied to a salt–solvent system.

(7) Breslow, R.; Guo, T. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 167.

(8) Mayer, S. W. *J. Phys. Chem.* **1963**, *67*, 2160 and references cited therein. Also see ref 6a.

(9) Friedman, H. L.; Krishnan, C. V. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1973; Vol. 1, Chapter 1.

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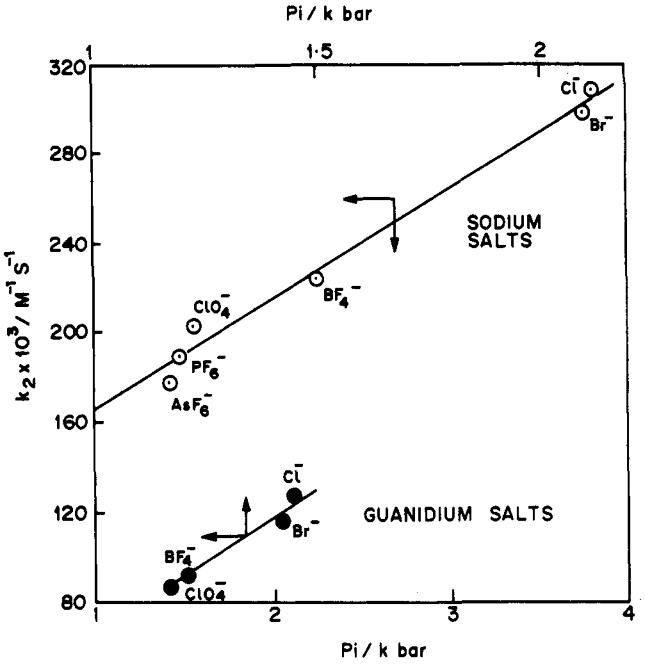

Figure 1. Rate constant, k_2, as a function of internal pressure, P_i, caused by 2 M salt solutions.

anions in conjunction with their interactions with water molecules as ion–water interactions. But since the cation–water interaction for sodium and guanidinium will not be the same, total effect produced by ion–water interactions of these salts will be different on the reaction rates. These interactions can be explained in terms of structure-making and -breaking effects which are qualitatively discussed in several places.[10] How the structure-making and -breaking effects can be quantified with respect to the kinetic profiles of the D–A reactions will be the subject of a future paper. The D–A reactions are accompanied by a negative volume of activation,[11] and thus, internal pressure produced by a salt solution should cause the rate of reaction[10a] to vary as a function of internal pressure.

In summary, we have provided an alternate explanation to describe the reaction rates in terms of internal pressure. We reiterate that internal pressure may not be the sole reason, but serves as one of the possibilities to explain the reaction rates.

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(10) (a) Dack, M. R. J. *J. Chem. Educ.* **1974**, *51*, 231. (b) Akitt, J. W. *J. Chem. Soc., Dalton Trans.* **1973**, 1446 and references of Akitt cited therein. (c) Frank, H. S. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1972; Vol. 1, Chapter 14. (d) Leyendekkars, J. V. *J. Chem. Soc.*, Faraday Trans. 1 **1983**, *79*, 1123.

(11) Van Eldik, R.; Asono, T.; Le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549.