

(7Z, 11E)-7, 11-Hexadecadien-1-ol THP ether(**12**). To a stirred solution of (11E)-11-hexadecen-7-yn-1-ol THP ether (**2**) (0.22g, 0.68 mmol) in methanol (3.0 ml) were added 5%-palladium on barium sulfate (28 mg) and quinoline (2 drops). The mixture was stirred under hydrogen atmosphere for 12hr and filtered to remove the catalyst. Methanol was evaporated in vacuo. The residue was extracted with ether and washed with 6N-HCl, water and brine. The organic layer was dried over MgSO₄ and concentrated in vacuo to give (7Z, 11E)-7, 11-hexadecadien-1-ol THP ether(**15**)(0.19g, 85%); IR (NaCl, Neat) 2900, 2850, 1630, 1450, 1350, 1200, 1140, 1120, 1040, 970, 900 cm⁻¹; ¹H-NMR δ 0.90 (t, 3H), 1.10-2.30 (m, 26H), 3.20-4.05 (m, 4H), 4.55(bS., 1H), 5.50-5.80 (m, 4H).

(7Z, 11E)-7, 11-Hexadecadien-1-yl acetate(**1**). To a stirred solution of (7Z, 11E)-7, 11-hexadecadien-1-ol THP ether (**12**)(0.14g, 0.43 mmol) in ethanol(10 ml) was added PPTS (11mg). The mixture was stirred at 55°C for 6hr. Ethanol was evaporated in vacuo and the residue was extracted with ether. The organic layer was washed with 6N-HCl, water and brine and dried over MgSO₄. Concentration in vacuo gave (7Z, 11E)-7, 11-hexadecadien-1-ol (0.10g, 93%); IR (NaCl, neat) 3300, 2900, 2850, 1635, 1450, 1050, 970 cm⁻¹; ¹H-NMR δ 0.90 (t, 3H), 1.10-1.80 (m, 12H), 1.81-2.30 (m, 8H), 2.40 (s, 1H), 3.55 (t, 2H, J=6Hz), 5.10-5.70 (m, 4H).

To a stirred solution of (7Z, 11E)-7, 11-hexadecadien-1-ol (0.070g, 0.29 mmol) in dry pyridine (2.0 ml) was added anhydrous acetic anhydride (0.036g). The mixture was stirred overnight at room temperature and poured into ice-water and extracted with ether. The organic layer was washed with satd. NaHCO₃ solution and brine and dried over MgSO₄. Concentration in vacuo and distillation on Kugelrohr (200°C, 3 mmHg) afforded (7Z, 11E)-7, 11-hexadecadien-1-yl acetate (**1**) (0.045g, 55%); IR (NaCl, neat) 2900, 2850, 1740, 1460, 1360, 1240, 1040, 970, 700 cm⁻¹; ¹H-NMR δ 0.90 (t, 3H), 1.10-1.80 (m, 20H), 2.05 (s, 1H), 3.99 (t, 2H, J=6Hz), 5.20-5.70 (m, 4H).

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References

1. K. W. Vick, H. C. F. Su, L. L. Sower, P. G. Mahany, and P. C. Drummond, *Experientia*, **30**, 17 (1974).
2. H. E. Hummel, L. K. Gaston, H. H. Shorey, R. S. Kaae, K. J. Byrne, and P. M. Silverstein, *Science*, **181**, 873 (1973).
3. K. Mori, M. Tominaga, and M. Matsui, *Tetrahedron*, **31**, 1846 (1975).
4. H. Disselnkötter, K. Eiter, W. Karl, and D. Wendisch, *Tetrahedron*, **32**, 1591 (1976).
5. T. Ishihara and A. Yamamoto, *Agric. Biol. Chem.*, **48**(1), 211 (1984).
6. H. J. Bestmann, K. H. Koschatzky, W. Stransky and O. Vostrowsky, *Tetrahedron Letters*, 353 (1976).
7. A. Hammoud and C. Descoins, *Bull. Soc. Chim. France. Part 2*, 299 (1978).
8. N. N. Joshi, V. R. Mamadapur, and M. S. Chadha, *Tetrahedron*, **40**, 3285 (1984).
9. (a) M. Julia, S. Julia, and R. Guéan, *Bull. Soc. Chim. France*, 1072 (1960); (b) M. Julia, S. Julia, and S-Y. Tchen, *Bull. Soc. Chim. France*, 1849 (1961); (c) M. Julia, J-M. Paris, *Tetrahedron Letters*, 3445 (1974).
10. R. T. Hrubiec and M. B. Smith, *J. Org. Chem.*, **49**, 431 (1984).
11. G. H. Posner and C. E. Whitten, *Tetrahedron Letters*, 4647 (1970).
12. N. Green, M. Jacobson, T. J. Henneberry, and A. N. Kishaba, *J. Med. Chem.*, **10**, 533 (1967). We prepared 7-octyn-1-ol THP ether(**4**) from 1,6-hexanediol. Treatment of 1,6-hexanediol with HBr followed by protection with DHP and PPTS gave the THP ether of bromohydrin, which was reacted with sodium acetylide to afford 7-octyn-1-ol THP ether(**4**).

Thermodynamic Analysis of the Hammett Reaction Parameter and Free Energy Relationship for the Pressure Change

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Pressure dependance of Hammett reaction parameter was analyzed and the free energy relationship for the pressure change derived thermodynamically. There are insufficient data in the literature to test the relation derived but from some limited previous data it could be concluded that the parameter ρ is dependent on pressure and increase or decrease as pressure increase for a given reaction series.

Introduction

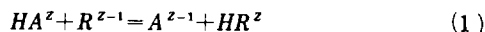
The empirical successes of the Hammett equation in correlating a wide variety of equilibrium and rate data are well known. Considerable progress has been made¹⁻⁶ in gaining some understanding of why the Hammett equation work as

well as it does, and also elucidating its thermodynamic consequences. Among the problems, temperature dependance of Hammett reaction parameter (ρ) was analyzed thermodynamically by Hepler⁷ and influence of pressure of ρ -parameter was discussed by Ellis and his coworkers.

In this study, probable effect of pressure on the Hammett

reaction constant ρ has been analyzed by thermodynamic method and discussed by the limited data from previous references. The temperature effect on the parameter are also predicted by simple derivation from Hammett equation.

Thermodynamic consequence of the Hammett Equation. The Hammett equation can be applied to the effect of substituents on the acid ionization as represented by the following reaction.



in which HA^Z is a substituted acid and HR^Z is a reference acid. If K denote the equilibrium constant of reaction (1), $K = K_{HA}/K_{HR}$. Then, Hammett equation can be expressed as

$$\log K = \rho \sigma \quad (2)$$

Thus we also have

$$\Delta G^\circ = -2.3RT\rho\sigma \quad (3)$$

in which $\delta \Delta G^\circ = \Delta G_{HA}^\circ - \Delta G_{HR}^\circ$. Hammett equation has also been applied similarly to substituent effects on equilibrium or rate constant for a wide variety of all other reaction. If we apply the equation to rate constant, $k = k_{subst}/k_{ref}$ and $\delta \Delta G^\circ$ must be used instead of K and $\delta \Delta G^\circ$.

If a general observation that the Hammett equation can be applied as well to one temperature and pressure as another. Therefore, we shall begin our discussion on the basis that eq.(2) is exactly varied over the entire temperature and pressure ranges of interest. According to the original meaning of the parameters in Hammett equation, the substituent parameter σ is independent on temperature and pressure, while reaction parameter ρ may depend on temperature and pressure as well as solvent or its surroundings. This relation can be denoted in aqueous solution as following,

$$\rho = \rho^*(T) = \rho(T, P) \quad (4)$$

The simple temperature dependence of ρ -parameter can be easily derived from

(i) linear free energy relationship

$$\delta(\Delta H^\circ) = \beta \delta(\Delta S^\circ) \quad (5)$$

$$\begin{aligned} \delta(\Delta G^\circ) &= \delta(\Delta H^\circ) - T\delta(\Delta S^\circ) \\ &= \beta \delta(\Delta S^\circ) - T\delta(\Delta S^\circ) = (\beta - T)\delta(\Delta S^\circ) \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{\delta(\Delta G_{T_1}^\circ)}{\delta(\Delta G_{T_2}^\circ)} &= \frac{(\beta - T_1)\delta(\Delta S_{T_1}^\circ)}{(\beta - T_2)\delta(\Delta S_{T_2}^\circ)} \\ \frac{-2.3RT_1\rho_{T_1}\sigma}{-2.3RT_2\rho_{T_2}\sigma} &= \frac{(\beta - T_1)\delta(\Delta S_{T_1}^\circ)}{(\beta - T_2)\delta(\Delta S_{T_2}^\circ)} \\ \rho_{T_1}/\rho_{T_2} &= \frac{(1 - \beta/T_1)\delta(\Delta S_{T_1}^\circ)}{(1 - \beta/T_2)\delta(\Delta S_{T_2}^\circ)} \end{aligned} \quad (7)$$

In general the entropy change is not so great in the experimental temperature range. Then, we can put $\delta(\Delta S_{T_1}^\circ) = \delta(\Delta S_{T_2}^\circ)$. The relation (7) can simply express as (8)

$$\rho_{T_1}/\rho_{T_2} = (1 - \beta/T_1)/(1 - \beta/T_2)$$

or

$$\rho = \rho_\infty(1 - \beta_1/T) \quad (8)$$

which is a simple relation derived from Jaffe.⁹

(ii) Thermodynamic analysis of the temperature dependence was treated by Hepler.

Differentiation of equation (2) with respect to temperature and combination of the resulting equation with well known thermodynamic equations leads to a number of further equations

$$\delta(\Delta H^\circ) = 2.3RT^2(\partial\rho/\partial T)_P\sigma \quad (9)$$

$$\delta(\Delta S^\circ) = 2.3R[\rho + T(\partial\rho/\partial T)_P]\sigma \quad (10)$$

$$\delta(\Delta H^\circ) = \frac{T^2(\partial\rho/\partial T)_P}{\rho + T(\partial\rho/\partial T)_P} \delta(\Delta S^\circ) \quad (11)$$

$$\delta(\Delta C_p^\circ) = 2.3R\sigma[T^2(\partial^2\rho/\partial T^2) + 2T(\partial\rho/\partial T)_P] \quad (12)$$

If we solve the equation (12) for ρ ,

$$\rho = \rho^*[1 - \beta^*/T + \frac{\delta(\Delta C_p^\circ)}{2.3R\sigma\rho^*} \ln T] \quad (13)$$

This is the general relation of ρ -parameter with the temperature. For the special case of $\delta(\Delta C_p^\circ) = 0$, equation (13) reduced to the equation (8) with $\rho_\infty = \rho^*$ and $\beta_1 = \beta^*$.

Substitution $\rho, (\partial\rho/\partial T)_P$ and $(\partial^2\rho/\partial T^2)_P$ from eq. (13) or (8) into eq. (11) give us the extrathermodynamic equation

$$\delta(\Delta H^\circ) = \left[\frac{\beta^* + \frac{T\delta(\Delta C_p^\circ)}{2.3R\sigma\rho^*}}{1 + \frac{\delta(\Delta C_p^\circ)}{2.3R\sigma\rho^*}} \right] \delta(\Delta S^\circ) \quad (14)$$

or

$$\delta(\Delta H^\circ) = \beta_1 \delta(\Delta S^\circ), \text{ when } \delta(\Delta C_p^\circ) = 0 \quad (15)$$

(iii) Influence of pressure on the ρ -parameter was derived from eq. (3) by Ellis and his coworkers⁸.

$$(\partial\rho/\partial P)_T = -\partial(\Delta V^\circ)/2.3RT\sigma \quad (16)$$

In the special case of $\delta(\Delta V^\circ) = \text{constant}$, ρ -parameter is linearly proportional to the pressure

$$\rho = \frac{-\delta(\Delta V^\circ)}{2.3RT\sigma} P + C$$

$$\rho(P) = -\frac{\delta(\Delta V^\circ)}{2.3RT\sigma} P + C \quad (17)$$

Thermodynamic Derivation of Hammett Reaction Parameter and Extrathermodynamic Equation for the Pressure Change.

(iv) In this case we take also similar assumption to that of temperature dependence, i.e. ρ depends on pressure but substituent parameter σ is independent on pressure. In the appropriate pressure range it can be supposed that there isn't significant structural distortion in the progress of reaction but solvent environments are easily affected by pressure change as in the case of temperature change.

To obtain the pressure effect of ρ -parameter, eq. (9) and (10) differentiate again with pressure partially.

$$\delta(\Delta H^\circ)' = \frac{\partial(\delta\Delta H^\circ)}{\partial P} = 2.3RT^2(\partial^2\rho/\partial T\partial P)\sigma \quad (18)$$

$$\delta(\Delta S^\circ)' = \frac{\partial(\delta\Delta S^\circ)}{\partial P} = 2.3R[(\partial\rho/\partial P) + T(\partial^2\rho/\partial T\partial P)]\sigma \quad (19)$$

From eq. (18) and (19), we can get the eq. (20)

$$\begin{aligned} \frac{\partial (\delta \Delta H^\circ)}{\partial P} &= T^2 (\partial^2 \rho / \partial T \partial P) / [(\partial^2 \rho / \partial P) \\ &+ T (\partial^2 \rho / \partial T \partial P)] \frac{\partial (\delta \Delta S^\circ)}{\partial P} \\ \delta (\Delta H^\circ)' &= [T^2 (\partial^2 \rho / \partial T \partial P) / (\frac{\partial \rho}{\partial P}) + T (\frac{\partial^2 \rho}{\partial T^2 P})] \delta (\Delta S^\circ)' \end{aligned} \quad (20)$$

To solve the upper eq. (20), some thermodynamic modification are necessary

$$\begin{aligned} \partial (\Delta H^\circ)' &= d(\delta \Delta H^\circ) / dP = T d(\delta \Delta S^\circ) / dP + \delta (\Delta V^\circ) \\ &= -T \left(\frac{d\delta (\Delta V^\circ)}{dT} \right) + \delta (\Delta V^\circ) \end{aligned}$$

$$\delta (\Delta H^\circ)' = -\delta (\Delta V^\circ) (T \delta (\Delta \kappa^\circ) - 1),$$

where

$$\delta (\Delta \kappa^\circ) = \frac{1}{\delta (\Delta V^\circ)} \left[\frac{\partial \delta (\Delta V^\circ)}{\partial T} \right]_P \quad (21)$$

Substitution of eq. (18) into eq.(21) gives

$$2.3RT^2 (\partial^2 \rho / \partial P \partial P) \sigma = -\delta (\Delta V^\circ) (T \delta (\Delta \kappa^\circ) - 1) \quad (22)$$

and from eq. (13)' second derivation of ρ are calculated as follows;

$$\begin{aligned} \rho (T, P) &= \rho^*(P) \left[1 - \beta^*/T + \frac{\delta (\Delta CP^\circ)}{2.3R\sigma\beta^*(P)} \ln T \right] \\ \left(\frac{\partial \rho}{\partial T} \right)_P &= \rho^*(P) \left[\frac{\beta^*}{T^2} + \frac{\delta (\Delta CP^\circ)}{2.3R\sigma\beta^*(P)T} \right] \\ \frac{\partial^2 \rho}{\partial T \partial P} &= \left(\frac{d\rho^*}{dP} \right)_T \left[\frac{\beta^*}{T^2} + \frac{\delta (\Delta CP^\circ)}{2.3R\sigma\beta^*(P)T} \right] \\ &+ \rho^* \left[-\frac{\delta (\Delta CP^\circ)}{2.3R\sigma\beta^*(P)T} \left(\frac{\partial \rho^*}{\partial P} \right)_T \right] \\ \frac{\partial^2 \rho}{\partial T \partial P} &= \frac{\beta^*}{T^2} \left(\frac{\partial \rho^*}{\partial P} \right)_T \end{aligned} \quad (23)$$

Putting the eq. (23) into the eq. (22) gives

$$2.3RT^2 \left\{ \frac{\beta^*}{T^2} \left(\frac{\partial \rho^*}{\partial P} \right)_T \right\} \sigma = -\delta (\Delta V^\circ) (T \delta (\Delta \kappa^\circ) - 1)$$

$$\frac{d\rho^*}{dP} = -\frac{\delta (\Delta V^\circ)}{2.3R\sigma\beta^*} (T \delta (\Delta \kappa^\circ) - 1)$$

$$d\rho^*(P) = -\frac{\delta (\Delta V^\circ)}{2.3R\sigma\beta^*} (T \delta (\Delta \kappa^\circ) - 1) dP$$

or

$$\rho^*(P) = -\frac{\delta (\Delta V^\circ)}{2.3R\sigma\beta^*} (T \delta (\Delta \kappa^\circ) - 1) P + C \quad (24)$$

Since the reaction parameter ρ is an arbitrary value, constant C can be put arbitrary as C=0.

$$\rho^*(P) = -\frac{\delta (\Delta V^\circ)}{2.3R\sigma\beta^*} (T \delta (\Delta \kappa^\circ) - 1) P \quad (25)$$

Insertion of eq. (25) into eq. (13) or (13)', we can get the final result that Hammett reaction parameter ρ is a function of temperature and pressure.

$$\begin{aligned} \rho (T, P) &= -\frac{\delta (\Delta V^\circ)}{2.3R\sigma\beta^*} (T \delta (\Delta \kappa^\circ) - 1) P \times \\ &\left[1 - \frac{\beta^*}{T} + \frac{\delta (\Delta CP^\circ)}{2.3R\sigma\beta^*} \ln T \right] \end{aligned} \quad (26)$$

Accuracy of most experimental data is such that we are limited to consideration of both $\delta (\Delta H^\circ)$ and $\delta (\Delta S^\circ)$ as temperature independent constants. It therefore follows from $d\delta (\Delta H^\circ) / dT = \delta (\Delta CP^\circ)$ and $d\delta (\Delta S^\circ) / dT = \delta (\Delta CP^\circ) / T$ that in these common cases we must take $\delta (\Delta CP^\circ) = 0$. From eq. (26) we therefore have

$$\rho (T, P) = -\frac{\delta (\Delta V^\circ)}{2.3R\sigma\beta^*} (T \delta (\Delta \kappa^\circ) - 1) P \left(1 - \frac{\beta^*}{T} \right) \quad (27)$$

$$\rho (T, P) = \rho_\infty P \left(1 - \frac{\beta^*}{T} \right) \quad (28)$$

where

$$\rho_\infty = -\frac{\delta (\Delta V^\circ)}{2.3R\sigma\beta^*} (T \delta (\Delta \mu^\circ) - 1)$$

To obtain the free energy relationship, differentiate eq. (28) with T and P and cross derivative

$$\partial \rho / \partial T = \rho_\infty P \frac{\beta^*}{T^2}$$

$$\partial \rho / \partial P = \rho_\infty (1 - \beta^*/T)$$

$$\frac{\partial^2 \rho}{\partial T \partial P} = \rho_\infty \frac{\beta^*}{T^2}$$

and the results put into eq. (20)'

$$\begin{aligned} \delta (\Delta H^\circ)' &= \left[\frac{T^2 \rho_\infty \beta^* / T^2}{\rho_\infty (1 - \beta^*/T) + T \rho_\infty \beta^* / T^2} \right] \delta (\Delta S^\circ)' \\ \delta (\Delta H^\circ)' &= \beta^* \delta (\Delta S^\circ)' \end{aligned} \quad (29)$$

Eq. (29) is a linear free energy relationship for the pressure change and the result is just the same as for the substituents except for $\delta (\Delta H^\circ)'$ and $\delta (\Delta S^\circ)'$ instead of $\delta (\Delta H^\circ)$ and $\delta (\Delta S^\circ)$. Comparing the our result eq. (25) with eq. (17);

$$\rho^*(P) = -\frac{\delta (\Delta V^\circ)}{2.3R\sigma\beta^*} (T \delta (\Delta \kappa^\circ) - 1) P$$

$$\rho (P) = -\frac{\delta (\Delta V^\circ)}{2.3RT\sigma} P + C$$

both relations are almost the same result considering the ρ -parameter is arbitrary defined value and $\delta (\Delta \mu^\circ) = 0^{12}$. v) The another probable effect of temperature on the Hammett reaction constant is also derivable from the Hammett equation similar to Ellis' derivation for the pressure effect. Differentiation of eq. (3) with temperature gives eq. (30).

$$\rho = -\frac{\delta (\Delta G^\circ)}{2.3RT\sigma}$$

$$d\rho/dT = -\frac{1}{2.3R\sigma} \frac{d(\delta(\Delta G^\circ)/T)}{dT}$$

$$= -\frac{1}{2.3R\sigma} \left[\frac{1}{T} \frac{d\delta(\Delta G^\circ)}{dT} + \delta(\Delta G^\circ) \left(-\frac{1}{T^2}\right) \right]$$

$$= -\frac{1}{2.3R\sigma} \left[-\frac{\delta(\Delta H^\circ)}{T^2} \right]$$

$$= \frac{\delta(\Delta H^\circ)}{2.3R\sigma T^2}$$

$$d\rho = -\frac{\delta(\Delta H^\circ)}{2.3R\sigma T^2} dT$$

$$\rho = -\frac{\delta(\Delta H^\circ)}{2.3R\sigma T} + C \quad (30)$$

$$= \rho_\infty (1 - \beta/T) \quad (31)$$

where $C = \rho_\infty$ and $\beta = \frac{\delta(\Delta H^\circ)}{2.3R\sigma\rho_\infty}$

This result is just the same as previous result in eq. (8) and Hepler's derivation.

Excudation of the pressure effect on the hammett reaction parameter According to theoretical derivation of pressure and temperature effects on the Hammett reaction parameter (19), ρ -parameter is proportional to the pressure but inversely proportional to the temperature. The experimental identification of the pressure effect was attempted by Fisher, Mann, and Vaughan for some benzoic acids and phenylacetic acid⁹. Table 1 shows their results. It is clear from Table 1 that, in accord with prediction, ρ diminishes with increase in pressure. It may be assumed that the pressure increases and the solvent becomes more compressed, the contraction

Table 1. Influence of pressure on the Hammett reaction constant (ρ) from Fisher *et al.*

(a) Benzoic acids (H, p-NO₂, p-CH₃, m-OCH₃, m-F, m-NO₂, p-F)

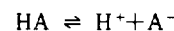
| Pressure (bar) | ρ | r |
|----------------|--------|-------|
| 1 | 1.039 | 1.000 |
| 500 | 1.013 | 1.000 |
| 1000 | 0.996 | 1.000 |
| 1500 | 0.979 | 1.000 |
| 2000 | 0.965 | 1.000 |
| 2500 | 0.954 | 0.999 |
| 3000 | 0.943 | 0.999 |

(b) Phenylacetic acids (H, m-NO, m-Cl, p-Cl, p-OCH, p-CH, m-F, p-F)

| Pressure (bar) | ρ | r |
|----------------|--------|-------|
| 1 | 0.491 | 0.999 |
| 1000 | 0.457 | 0.999 |
| 2000 | 0.434 | 0.998 |
| 3000 | 0.417 | 0.998 |

produced on ionization becomes smaller. Hence $\delta(\Delta V^\circ)$ is negative value and ρ decrease as pressure increase¹².

The $\delta(\Delta V^\circ)$ value is a difference of two volume change in dissociation reaction of reference (HR²) and substituted acid (HR²). Therefore, the extent and its positive or negative sign of $\delta(\Delta V^\circ)$ are dependent on the reactions. For example, $\delta(\Delta V^\circ)$ values of benzoic acids and phenylacetic acids are positive and the ρ -values are diminished as pressure increase. These concerned acids have the charge increase in the following type of ionization.



But some acids should have no net charge change, for example, reaction (32) or rather charge decrease and $\delta(\Delta V^\circ)$ have negative values. If the $\delta(\Delta V^\circ)$ is a negative value,



ρ -value will increase as the pressure increases. These phenomenon can't decide simply from the charge separation of single acid, because $\delta(\Delta V^\circ)$ is the difference of volume

Table 2. pKa and ρ -values for phenols at 25°C

(a) m- and p-substituted phenols

| Substituents | P = 1bar | 500 | 1000 | 1500 | 2000 |
|---------------------------------|---------------------|------|------|------|------|
| H | 9.98 ^a | 9.78 | 9.54 | 9.38 | 9.28 |
| m-NO ₂ | 8.38 ^b | 8.25 | 8.15 | 8.05 | 7.96 |
| p-NO ₂ | 7.16 ^b | 7.07 | 6.99 | 6.92 | 6.84 |
| p-Br | 9.52 ^c | 9.45 | 9.38 | 9.31 | 9.25 |
| m-CN | 8.57 ^{d,e} | | | | |
| p-CN | 7.97 ^{d,e} | | | | |
| p-Cl | 9.02 ^f | | | | |
| m-Cl | 9.40 ^{b,g} | | | | |
| m-I | 9.04 ^d | | | | |
| p-I | 9.34 ^h | | | | |
| m-Br | 9.03 ^g | | | | |
| m-CH ₃ | 10.10 ^g | | | | |
| p-CH ₃ | 10.17 ⁱ | | | | |
| m-C ₂ H ₅ | 10.70 ^g | | | | |
| p-C ₂ H ₅ | 10.00 ^j | | | | |
| m-OH | 8.98 ^g | | | | |

| | | ρ -values | | | |
|--|-------|-------------------|--------------|--|--|
| | 1 bar | $\rho(t) = 2.739$ | $r = 0.9318$ | | |
| | | $\rho(4) = 3.160$ | $r = 0.9415$ | | |
| | 500 | $\rho(4) = 3.085$ | $r = 0.9385$ | | |
| | 1000 | $\rho(4) = 2.941$ | $r = 0.9264$ | | |
| | 1500 | $\rho(4) = 2.880$ | $r = 0.9216$ | | |
| | 2000 | $\rho(4) = 2.859$ | $r = 0.9189$ | | |

(b) o-substituted phenols

| Substituents | P = 1bar | 500 | 1000 | 1500 | 2000 |
|----------------------------------|--------------------|------|------|------|------|
| H | 9.98 ^a | 9.78 | 9.54 | 9.38 | 9.28 |
| o-Cl | 8.52 ^c | 8.40 | 8.21 | 8.13 | 7.91 |
| o-NO ₂ | 7.28 ^b | 7.16 | 7.06 | 6.97 | 6.89 |
| o-Br | 8.45 ^e | | | | |
| o-I | 8.51 ^e | | | | |
| o-OC ₂ H ₅ | 10.11 ^e | | | | |
| o-CH ₃ | 10.20 ⁱ | | | | |
| o-C ₂ H ₅ | 10.20 ^j | | | | |

| | | ρ -Values | | | |
|--|-------|----------------------|--------------|--|--|
| | 1 bar | $\rho(t) = 1.9846$ | $r = 0.9014$ | | |
| | | $\rho(t-1) = 1.8954$ | $r = 0.9209$ | | |
| | | $\rho(3) = 1.8884$ | $r = 0.9142$ | | |
| | 500 | $\rho(3) = 1.8441$ | $r = 0.9207$ | | |
| | 1000 | $\rho(3) = 1.7214$ | $r = 0.9189$ | | |
| | 1500 | $\rho(3) = 1.7042$ | $r = 0.9240$ | | |
| | 2000 | $\rho(3) = 1.1644$ | $r = 0.8989$ | | |

change between reference and substituted acids. And the volume change in the dissociation reaction may express as the sum of two terms^{10,13,14}

$$\delta(\Delta V^\circ) = \delta(\Delta V^\circ)_s + \delta(\Delta V^\circ)_m \quad (33)$$

Where $\delta(\Delta V^\circ)_s$ is the relative volume change of the reacting molecules from reactants to products and $\delta(\Delta V^\circ)_m$ is the relative volume change of the solvent for the same conversion.

Generally $\delta(\Delta V^\circ)_m$ is not important in the case of dissociation reaction in polar solvent. Consequently there will be a pressure effect of ρ if only $\delta(\Delta V^\circ)_s$ is not negligible. Hamann¹¹ recognizes two factors contributing to $\delta(\Delta V^\circ)_s$

$$\delta(\Delta V^\circ)_s = \delta(\Delta V^\circ)_b + \delta(\Delta V^\circ)_e \quad (34)$$

where $\delta(\Delta V^\circ)_b$ is the relative volume change of the solvent resulting from rearrangement of the solvent molecules to accommodate the changed shape of the reacting molecules. $\delta(\Delta V^\circ)_e$ is similarly a relative volume change resulting from the electrostriction of the solvent to the reacting molecules. Hamann considers that the contribution of $\delta(\Delta V^\circ)_b$ to $\delta(\Delta V^\circ)_s$ is likely to be small and negligible. Thus, we are chiefly concerned with the effect of pressure on $\delta(\Delta V^\circ)_e$, the "polar" contribution to $\delta(\Delta V^\circ)_s$, because it is only the case of

Table 3. pKa and ρ -values for anilines at 25°C

(a) m- and p-substituted anilines

| Substituents | P=1bar | 500 | 1000 | 1500 | 2000 |
|---------------------------------|---------------------|-------|------------------|------------|-------|
| H | 4.855 ^a | 4.893 | 4.915 | 4.935 | 4.955 |
| m-NO ₂ | 2.43 ^m | 2.48 | 2.53 | 2.57 | 2.61 |
| p-NO ₂ | 1.01 ^m | 1.06 | 1.11 | 1.16 | 1.20 |
| m-OCH ₃ | 4.22 ⁿ | | | | |
| m-CN | 2.75 ⁿ | | | | |
| p-OCH ₃ | 5.34 ^o | | | | |
| m-Cl | 3.52 ^{o,p} | 1 bar | ρ -values | | |
| p-Cl | 3.98 ^o | | $\rho(3)=3.5115$ | $r=0.9640$ | |
| m-I | 3.59 ^{o,p} | 500 | $\rho(3)=4.3175$ | $r=0.9569$ | |
| p-I | 3.79 ^o | 1000 | $\rho(3)=4.3015$ | $r=0.9565$ | |
| m-Br | 3.53 ^p | 1500 | $\rho(3)=4.2641$ | $r=0.9556$ | |
| p-Br | 3.89 ⁱ | 2000 | $\rho(3)=4.2298$ | $r=0.9555$ | |
| m-CH ₃ | 4.72 ^o | | $\rho(3)=4.2030$ | $r=0.9548$ | |
| p-CH ₃ | 5.10 ^q | | | | |
| m-C ₂ H ₅ | 4.70 ⁿ | | | | |

(b) o-substituted anilines

| Substs. | 1bar | 500 | 1000 | 1500 | 2000 |
|---------|-----------------------|--------|------------------|------------|--------|
| o-CH | 4.57 ^a | 4.66 | 4.69 | 4.76 | |
| o-NO | -0.230 ^m | -0.197 | -0.161 | -0.132 | -0.104 |
| o-OCH | 4.52 ^m | | | | |
| o-Cl | 2.65 ⁱ | | | | |
| o-I | 2.60 ⁱ | | | | |
| o-Br | 2.53 ^{i,o,r} | 1 bar | ρ -values | | |
| | | | $\rho(t)=3.1099$ | $r=0.9799$ | |
| | | 500 | $\rho(2)=3.4532$ | | |
| | | 1000 | $\rho(2)=3.4942$ | | |
| | | 1500 | $\rho(2)=3.4899$ | | |
| | | | $\rho(2)=3.5194$ | | |

Table 4. pKa and ρ -values for pyridinos at 25°C

(a) m- and p-substituted pyridines

| Substs. | P=1bar | 500 | 1000 | 1500 | 2000 |
|---------------------------------|-------------------|------|------|------|------|
| m-CN | 1.35 ^s | 1.36 | 1.37 | 1.38 | 1.39 |
| p-CN | 1.89 ^s | 1.92 | 1.91 | 1.93 | 1.94 |
| m-Cl | 2.84 ^t | 2.89 | 2.94 | 3.02 | 3.07 |
| m-Br | 2.84 ^t | 2.89 | 2.97 | 3.04 | 3.09 |
| m-I | 3.25 ^v | | | | |
| m-CH ₃ | 5.64 ^u | 5.67 | 5.70 | 5.73 | 5.74 |
| p-CH ₃ | 5.94 ^u | 5.97 | 6.00 | 6.02 | 6.04 |
| m-C ₂ H ₅ | 5.59 ^w | 5.62 | 5.64 | 5.66 | 5.68 |
| p-C ₂ H ₅ | 5.81 ^u | 5.83 | 5.84 | 5.86 | 5.87 |
| m-NH ₂ | 5.93 ^s | 5.97 | 6.01 | 6.06 | 6.10 |
| p-NH ₂ | 9.11 ^s | 9.17 | 9.23 | 9.28 | 9.32 |
| H | 5.2 ^u | | | | |

| ρ -values | | |
|----------------|-------------------|------------|
| 1 bar | $\rho(t)=5.7566$ | $r=0.9926$ |
| | $\rho(10)=5.7854$ | 0.9926 |
| 500 | $\rho(10)=5.7982$ | 0.9923 |
| 1000 | $\rho(10)=5.8178$ | 0.9924 |
| 1500 | $\rho(10)=5.8184$ | 0.9922 |
| 2000 | $\rho(10)=5.8235$ | 0.9920 |

(b) o-substituted pyridines

| Substs. | P=1bar | 500 | 1000 | 1500 | 2000 |
|---------------------------------|-------------------|------|------|------|------|
| H | 5.20 ^a | | | | |
| o-Br | 2.73 ^t | 2.79 | 2.84 | 2.92 | 2.97 |
| o-Cl | 2.51 ^s | 2.51 | 2.50 | 2.49 | 2.48 |
| o-CH ₃ | 5.93 ^u | 5.95 | 6.00 | 6.00 | 6.04 |
| o-I | 1.82 ^r | | | | |
| o-OCH ₃ | 3.06 ^r | | | | |
| o-C ₂ H ₅ | 5.89 ^u | 5.91 | 5.93 | 5.95 | 5.95 |

| ρ -Values | | |
|----------------|--------------------|------------|
| 1 bar | $\rho(t)=8.1450^*$ | $r=0.9740$ |
| | $\rho(4)=6.2573^*$ | 0.9773 |
| 500 | $\rho(4)=7.4890$ | 0.9821 |
| 1000 | $\rho(4)=7.5141$ | 0.9799 |
| 1500 | $\rho(4)=7.4598$ | 0.9787 |
| 2000 | $\rho(4)=7.4474$ | 0.9757 |

* $\rho(t)$; all substituents $\rho(4)$; 4-substituents

^a J. U. Hwang *et al.*, *J. Kor. Chem. Soc.*, **26** 311 (1983). ^b S. D. Hamann M. Linton, *J. Chem. Soc., Farad.* **1**, **70** 2239 (1974). ^c J. U. Hwang *et al.*, Annual Report (1984), Ministry of Ed, Korea. ^d P. D. Bolton, F. M. Hall and I. H. Reece, *Spectrochimica Acta.*, **22** 1825 (1966). ^e H. C. Ko, W. F. O'Hara, T. Hu and L. G. Hepler, *J. Am. Chem. Soc.*, **86** 1003 (1964). ^f C. N. Judson and M. K. Kilpatrick, *J. Am. Chem. Soc.*, **71** 3110 (1949). ^g P. D. Bolton, F. M. Hall and I. H. Reece, *J. Chem. Soc. (B)* 709 (1967). ^h P. D. Bolton, F. M. Hall and I. H. Reece, *Spectrochimica Acta*, **22** 1140 (1966). ⁱ R. C. Weast ed., "Handbook of Chemistry and Physics" 61 edition, Chemical Rubber Co., Cleveland, Ohio (1981). ^j C. Galumbic, Orchin, Weker, *J. Amer. Chem. Soc.*, **71** 2624 (1949). ^k L. P. Fernandes and L. G. Hepler, *J. Am. Chem. Soc.*, **81** 1783 (1959). ^l P. D. Bolton, F. M. Hall and I. H.

Reece, *J. Chem. Soc. (B)*, 717 (1966). ^m S. D. Hamann and M. Linton, *J. Chem. Soc. Faraday 1*, **71** 485 (1975). ⁿ A. Bryson, *J. Am. Chem. Soc.*, **82** 4858 (1960). ^o A. I. Biggs, *J. Chem. Soc.*, 257 (1961). ^p P. D. Bolton and F. M. Hall, *Austl. J. Chem. Soc.*, **21** 939 (1968). ^q C. Golumbic and G. Goldbach, *J. Am. Chem. Soc.*, **73** 3966 (1951). ^r J. Christensen, M. Izatt, P. Wrathall and L. D. Hansen, *J. Chem. Soc. (A)*, 1212 (1969). ^s J. U. Hwang, J. J. Chung, J. E. Lee, *J. Kor. Chem. Soc.*, **30** (2) 145 (1986). ^t J. U. Hwang *et al.*, *J. of Kyungpook Univ.*, **38** 85, 97 (1984). ^u J. U. Hwang, J. E. Lee, J. W. Jung and K. H. Chang, *J. Kor. Chem. Soc.*, **30**(2) 159 (1986). ^v H. C. Brown and X. R. Mihm, *J. Am. Chem. Soc.*, **77** 1723 (1955).

$\delta(\Delta V)_{\rho}^{\ddagger} \cdot O$ that we expect an appreciable pressure effect on ρ . From our discussion, we conclude that the effect of pressure on the ρ -parameter can't be decided simply from glancing reacting substance, but it depends on reaction series, solvent, net charge change and etc. In this study we attempted to test the theoretical result with experimental data. But there are not sufficient data in the literature at high pressure. Table 2 shows for the phenol derivatives.

There are enough data at atmospheric pressure but only several substituents at high pressure. From these insufficient data we can't discuss fully but only the tendency of the pressure effect on ρ -parameter. It is clear from Table (2), in accordance with prediction. ρ values diminishes with increase in pressure inspite of low r-value. Table 3 and 4 show for the anilines and pyridines.

Pyridines have relatively enough data and $r=0.992$. In pyridines and o-substituted aniline, ρ -values increase with increase in pressure.

As mentioned previously, the effects of pressure on Hammett reaction parameter ρ are affected the various situation

i.e.net charge change, solvation, solvent structure, copresibility, reaction series and etc.

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References

1. L. D. Hammett, "Physical Organic Chemistry" 2nd ed. McGrawHill, New York, N. Y. (1970).
2. J. E. Leffler and E. Grunwald, "Rates and Equilibrium of Organic Reactions" John Wiley and Sohn Inc. New York, N. Y. (1963).
3. P. D. Bolton and L. G. Hepler, *Quart. Rev. Chem. Soc.*, **25** 521 (1971).
4. L. G. Hepler, *J. Am. Chem. Soc.*, **85** 3089 (1963).
5. J. W. Larson and L. G. Hepler, *J. Org. Chem.*, **33** 3961 (1968).
6. J. W. Larson and L. G. Hepler, "Ion Solvent Interaction" ed. by J. F. Coetzee and C. D. Ritchie, Marol Dekkar Inc. New York, N. Y. (1969).
7. L. G. Hepler, *Can. J. Chem. Soc.*, **49** 2803 (1971).
8. A. J. Ellis, W. S. Fyfe, R. I. Rutherford, A. Fischer and J. Vaughan, *J. Chem. Phys.* **31** 176 (1959).
9. A. Fischer, B. R. Mann and J. Vaughan, *J. Chem. Soc.*, 1093 (1961).
10. M. G. Evans and M. Polanyi, *Trans. Farad. Soc.*, **31** 875 (1935).
11. S. D. Hamann, "Physicochemical Effects of Pressure" Butterworths Scientific Pub. Co., London (1957).
12. B. S. El'yanov and S. D. Hamann, *Austl. J. Chem. Soc.*, **28** 945 (1975).
13. N. A. North, *J. Phys. Chem.*, **77** 931 (1973).
14. S. D. Hamann and S. C. Lim, *Austl. J. Chem. Soc.*, **7** 329 (1954).

Competitive Photochlorination Reactions of Silane, di-Chloro and tri-Chlorosilanes at 337.1 nm

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The hydrogen abstraction reactions of SiH_4 , SiH_2Cl_2 and SiHCl_3 by ground state chlorine atoms generated photochemically from chlorine molecules have been studied at temperatures between 15 and 100°C. The absolute rates for the reactions have been obtained by a competition technique using ethane as a competitor. The rate expressions (in $\text{cm}^3/\text{mol}/\text{s}$) are found to conform to an Arrhenius rate law: $k_{\text{SiH}_4} = (7.98 \pm 0.42) \times 10^{13} \exp[-(1250 \pm 20)/T]$. $k_{\text{SiH}_2\text{Cl}_2} = (2.25 \pm 0.12) \times 10^{15} \exp[-(1010 \pm 10)/T]$. $k_{\text{SiHCl}_3} = (9.04 \pm 0.28) \times 10^{14} \exp[-(1200 \pm 10)/T]$. The activation energies obtained from this study represent the same trend as with the carbon analogues, while this trend was not found with respect to the bond dissociation energies among silicon compound homologues. These anomalous behaviors were interpreted in terms of electronic effects and of the structural differences between these compounds.

Introduction

The reactions of the abstraction of hydrogen from

hydrocarbon molecules have been studied extensively using chlorine atoms during the last decade. However, despite the long history of these investigations, such attempts with their