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Temperature and Pressure Effects on the Reversible Reaction of a Parent Phenol (GH) Corresponding to Galvinoxyl with Aliphatic Amines

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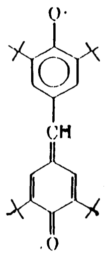
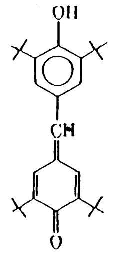
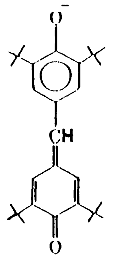
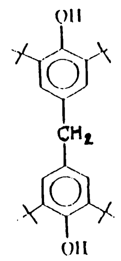
The effects of temperature and pressure on the reversible reaction between GH and aliphatic amines in acetonitrile have been studied spectrophotometrically. The formation of free ions rather than that of ion pairs has been confirmed by the modified Benesi–Hildebrand (B–H) plot. From the plot the equilibrium constants were estimated. From the temperature dependence of the equilibrium constant (K), the heat and entropy of reactions were estimated to be: $(\Delta H^\circ)_{av}=-44.5$ kJ mol^{-1}, and $(\Delta S^\circ)_{av}=-193$ J K^{-1} mol^{-1}. From the pressure dependence of K the reaction volume $(\Delta V^\circ)_{av}$ was estimated to be -40 dm^3 mol^{-1}. When unbranched primary amines were used, a side reaction took place for which an explanation has been given.

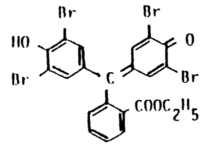
Phenoxyl radicals, sterically blocked by *t*-butyl groups in the 2,6-positions can often exist in solution as stable monomers. Of these radicals, so-called galvinoxyl (G•) is especially interesting in that although self-coupling is prohibited, it can act as a radical scavenger of unstable radicals[1] or abstract hydrogen from phenols.[2] In spite of a lot of data are available for G•, its parent compound "hydrogalvinoxyl (GH)" (2,6-di-*t*-butyl-4-(3,5-di-*t*-butyl-4-hydroxybenzylidene)-2,5-cyclohexadien-1-one) has been scarcely studied. This compound is a kind of phenol and easily dissociates into the corresponding phenolate ion in the presence of strong bases.[3] The anion (G$^-$) exhibits very deep color (λ_{max} ca. 580 nm).


G•


GH


G$^-$


GH$_3$


TBPE

Recently, we have studied the effects of temperature and pressure on the ionization reactions between triphenylmethane dye TBPE and amines.[4] We found that ionization takes place only in polar solvents and the equilibrium is scarcely sensitive to temperature and pressure. Since usual ionization reactions are accompanied by large negative values of ΔH° and ΔV°, the above findings are very curious and reasonable explanation is required. In this situation, it would be worthwhile to examine whether similar phenomenon is observed or not for similar systems for which symmetrical dispersal of negative charge in the resonance canonical forms can be expected. As a representative substance, we chose GH and investigated the temperature and pressure effects on the reversible reaction between GH and various kinds of aliphatic amines, since G$^-$ can be regarded as similar to TBPE anion in the sense just described above.

Experimental

Materials. Hydrogalvinoxyl(GH) and trihydrogalvinoxyl(GH$_3$) were prepared by the procedure of Adam and Cieu.[5] The purity was checked by melting point and 200 MHz ^{1}H NMR. Reagent-grade amines were dried over KOH and were distilled under reduced pressures. Reagent-grade acetonitrile was dried over molecular sieves (Wako Pure Chemicals 4A 1/16) followed by distillation and was stored under nitrogen atmosphere.

Measurements. Preparation of solutions were made at 25 °C, and the concentrations at other temperatures and pressures were corrected by using available data.[6] Spectra of G$^-$ and GH at 0.1 MPa were recorded on a Union SM-401 spectrophotmeter. A high-pressure vessel[7] with an especially-designed quartz cell (Fig. 1) was used for measurements under high pressures. It was set in a Hitachi 100-50 double-beam spectrophotometer. In both cases, the temperature of solution was regulated within ±0.1 °C using a thermocontroller.

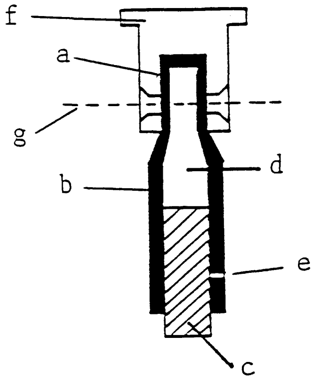


Fig. 1. Optical cell for measurements at high pressures. a, Flat qualtz cell; b, cylinder part of the cell; c, piston; d, sample solution; e, air outlet; f, cell holder; g, light path.

Results and Discussion

Estimation of Equilibrium Constants at 0.1 MPa. In the light of acid-base reactions generally known, our system could be expressed by

$$\mathrm{GH} + \mathrm{Am} \rightleftharpoons \underset{\text{ion pair}}{[\mathrm{G}^{-}\cdots\mathrm{AH}^{+}]} \rightleftharpoons \mathrm{G}^{-} + \mathrm{AmH}^{+} \qquad (1)$$

If the ion pair is formed predominantly with much less amount of the free ions, we can estimate the equilibrium constant defined by K=[ion pair]$_e$/[GH]$_e$[Am]$_e$ by applying the B–H equation[8] with amines (Am) in great excess over GH

$$[\mathrm{GH}]_0/A = (1/\varepsilon K)(1/[\mathrm{Am}]_0) + 1/\varepsilon \qquad (2)$$

where A is the absorbance at 580 nm due to G$^-$ with a cell of 1 cm light-path length. It was confirmed that there is no contribution of species other than G$^-$ to the absorbance.

Most proton-transfer reactions have been believed to produce ion-pair products in aprotic polar and nonpolar solvents. The linearity of the usual B–H plot has been regarded as evidence of its validity. Therefore, most authors are convincing of negligible amount of ionic dissociation of the ion-pair products.[9–11] For example, Sugimoto and co-workers[9] reported that proton is transferred from 2,4,6-trinitrotoluene to 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to form an ion pair instead of separate ions in 1,2-dichloroethane as well as acetonitrile. Their conclusion is based on the linear B–H plot of the type of Eq. 2. Recently, however, Gatezowski and Jarczewski[12] have cast suspicions for the formation of ion pair and hence the manipulation of the kinetic data. By means of the conductivity measurements together with the B–H plot, they examined the kinetic and thermodynamic data for the proton transfer reaction of 1-nitro-1-(4-nitrophenyl)alkanes with DBU in acetonitrile, and have concluded that at least 97% of the product dissociates into free ions. If it is the case, the equilibrium constant K is given by K=[G$^-$]$_e$[AmH$^+$]$_e$/[GH]$_e$[Am]$_e$, and modified B–H equation of the following type must be used.

$$[\mathrm{GH}]_0/A = (1/\varepsilon^2 K)(A/[\mathrm{Am}]_0) + 1/\varepsilon \qquad (3)$$

Using the same data, both types of the plot have been tested (Figs. 2 and 3). It is seen that each B–H plot according to Eq. 3 constitutes a good straight line with same intercepts, while each B–H plot on the basis of Eq. 2 is considerably curved. Hence we can unambiguously conclude that the formation of free ions is predominant in acetonitrile. A qualitative conductivity test was in favor of this conclusion. From the modified B–H plots, equilibrium constants for the reaction between GH and various kinds of amines were estimated at various temperatures. The average molar absorptivity was estimated to be 140000 dm^3 mol^{-1} cm^{-1}.

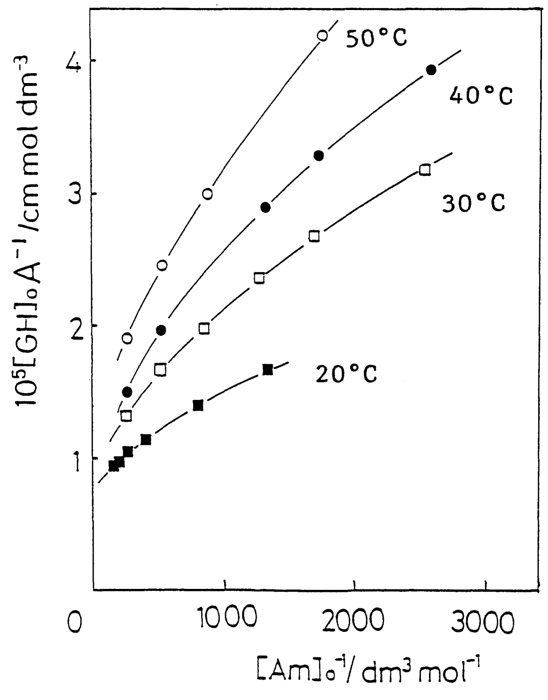


Fig. 2. Benesi-Hildebrand plot according to Eq. 2 for the reaction of GH with triethylamine.

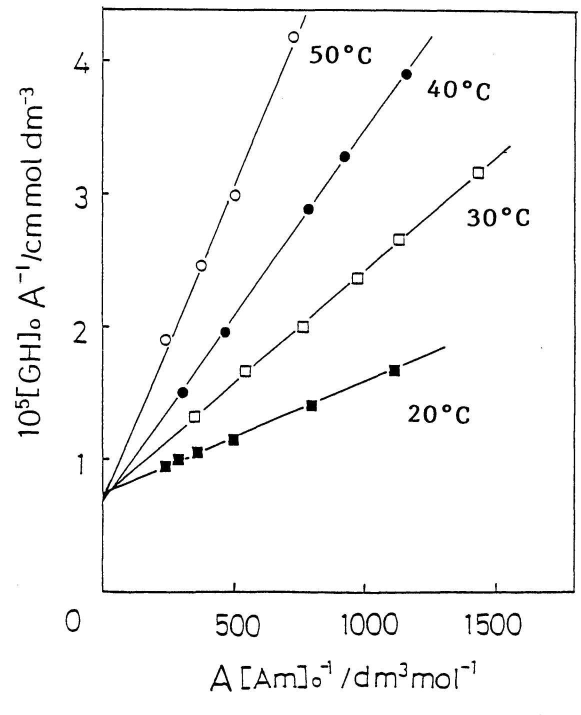


Fig. 3. Modified Benesi-Hildebrand plot according to Eq. 3.

However, when we used primary amines, the B–H plot by Eq. 3 was linear, but the estimated molar absorptivity was abnormally small (about 37500 dm^3 mol^{-1} cm^{-1}) except for t-butylamine. Moreover, the intensities due

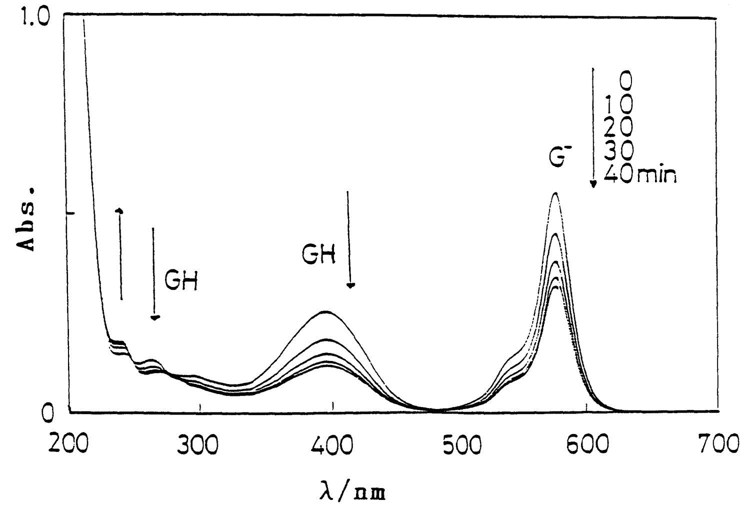


Fig. 4. Spectral change with time for the reaction between GH and hexylamine in acetonitrile at 25 °C; $[\mathrm{GH}]_0=1.19\times10^{-5}$ mol dm^{-3}, $[\mathrm{Am}]_0=2.32\times10^{-3}$ mol dm^{-3}.

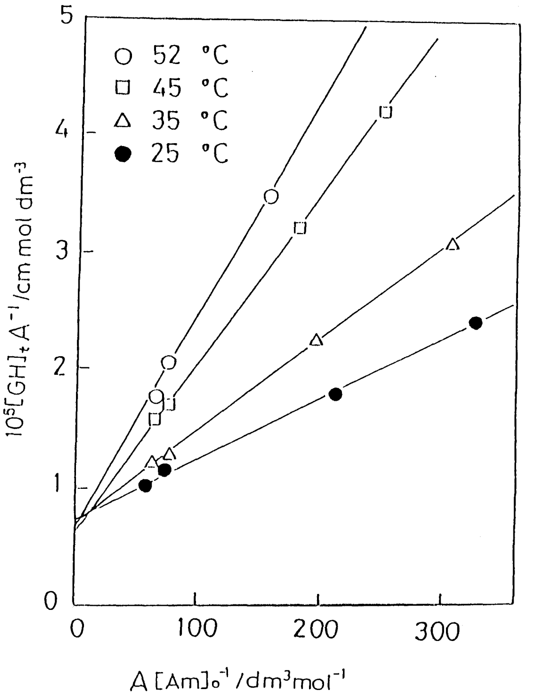


Fig. 5. Benesi–Hildebrand plot according to Eq. 3 for the reaction of GH with hexylamine; $[\mathrm{GH}]_t$ is defined by Eq. 4.

to GH and G$^-$ gradually decreased to reach a new equilibrium, and a new band appeared at 240 nm (Fig. 4). Therefore, it is likely that a side reaction is involved for this type of amines, and a part of GH is converted to a product X (see below). Hence, in place of initial concentration for GH, $[\mathrm{GH}]_t$ given by the following equation was used for the B–H plot.

$$[\mathrm{GH}]_t=[\mathrm{GH}]_e+[\mathrm{G}^-]_e \qquad (4)$$

Table 1. Equilibrium Constants at Various Temperature for the Reaction between Hydrogalvinoxyl and Aliphatic Amines

Amine[a]	10^3K			
	25 °C	35 °C	45 °C	55 °C
TEA	6.85(20°)	3.01(30°)	1.59(40°)	1.03(50°)
DEAE	1.25	0.823	0.567	0.374
DMAE	0.432	0.292	0.200	0.134
DPA	4.36	2.66	1.56	0.945
t-BA	1.25	0.755	0.470	0.283
PA	1.52	0.936	0.567	0.355
BA	1.52	0.929	0.609	0.375
HA	1.18	0.742	0.406	0.318(52°)

a) TEA: triethylamine; DEAE: 2-(diethylamino)ethanol; DMAE: 2-(dimethylamino)ethanol; DPA: dipropylamine; *t*-BA: *t*-butylamine; PA: propylamine; BA: butylamine; HA: hexylamine.

The right-hand side concentrations were estimated by using the molar absorptivity at 396 nm (30300) due to GH and that at 580 nm (140000) due to G$^-$. Representative one is shown in Fig. 5. The values of molar absorptivity at 580 nm estimated from the intercept agreed well with the above value within experimental errors. The equilibrium constants at various temperatures were determined in this manner and are given in Table 1.

Equilibrium Constants at High Pressures. The absorbances at 580 and 396 nm were measured at various pressures, and the equilibrium constants at 25 °C were estimated on the assumption that the molar absorptivities at these wavelengths do not change with pressure and they are given in Table 2. It is seen that the value of K is remarkably affected by pressure. From the pressure dependence on K, the volume of reaction can be given by the following equation:[13]

$$\Delta V^\circ=-RT(\partial \ln K/\partial p)_T-\Delta n\kappa RT \qquad (5)$$

Table 2. Equilibrium Constants at Various Pressures

P/MPa	10^3K (25 °C)						
	0.091	18.2	27.3	36.5	54.7	72.9	82
TEA	4.35		6.72		8.62		10.9
DEAE	1.25	1.69		2.16	2.74	3.42	
DMAE	0.436	0.555		0.725	0.928	1.20	
DPA	4.13	5.37		6.99	8.72	10.8	
t-BA	0.936	1.24		1.51	2.05	2.52	
PA	1.55	2.13		2.85	3.57	4.59	
BA	1.49	2.01		2.59	3.23	3.89	

Table 3. Thermodynamical Quantities for the Reaction between GH and Aliphatic Amines

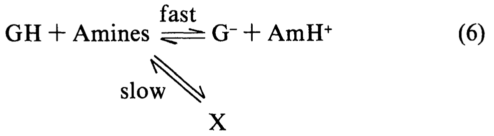
Amine	10^3K (298 K)	$\Delta H°$	$\Delta S°$	$\Delta V°$	pK_a
		kJ mol^{-1}	J K^{-1} mol^{-1}	dm^3 mol^{-1}	
TEA	4.35	−(48.8±2.1)	−(209±7)	−40.7	10.72
DEAE	1.25	−(37.8±0.7)	−(172±2)	−40.8	9.81
DMAE	0.432	−(36.8±0.6)	−(178±2)	−34.2	9.26
DPA	4.36	−(48.5±0.7)	−(195±2)	−38.2	11.00
t-BA	1.25	−(46.7±0.7)	−(200±2)	−35.4	10.83
PA	1.52	−(46.1±0.5)	−(196±2)	−44.4	10.57
BA	1.52	−(43.8±0.8)	−(190±2)	−42.9	10.63
HA	1.18	−(47.1±2.0)	−(202±5)	—	10.56

where κ denotes the isothermal compressibility of solution (=solvent), and Δn is the stoichiometrical change in the number of molecule accompanied by reactions. In the present case, Δn can be set as 0. Using the quadratic regression equation, $\ln K=a+bp+cp^2$, the partial molar volumes of reaction at 0.1 MPa were estimated.

The thermodynamical quantities are listed in Table 3, together with relevant data. These quantities could be regarded as normal in the light of organic acid-base reactions to form ion pair or separate ions, for which large negative values of $\Delta H°$, $\Delta S°$, and $\Delta V°$ due to solvation can be expected. In spite of this, K is much less than unity. The cause for this is, the $T\Delta S$-term overwhelms the ΔH-terms by more than 10 kJ mol^{-1}. The predominant role of the entropy term is in line with the large negative values of $\Delta V°$. The value of $\Delta V°$ can conventionally be attributed to the intrinsic volume change and the change in solvation. In the present case, the former contribution will be small, since only proton transfer takes place and there will be no serious stereochemical change. On the other hand, it has been generally recognized that ionization processes are accompanied by serious electrostriction around ions, which gives rise to a remarkable amount of volume shrinkage, as observed in the Menschutkin reactions. Especially, interactions between the aminium ions and acetonitrile through hydrogen bonding will play an important role.

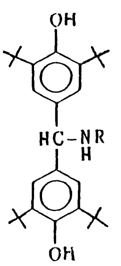
Very recently, we have reported that in TBPE–amine systems in polar solvents, K is scarecely sensitive to temperature and pressure[5] showing that the absolute values of $\Delta H°$, $\Delta S°$, and $\Delta V°$ are very small. The TBPE anion has a maximum absorption at ca. 600 nm in acetonitrile and the pattern of the band is very similar to that of G^-. Thus the electronic structure and hence the aspect of charge dispersal of the TBPE anion and G^- may be similar to each other. Therefore, it could be said that the abnormal thermodynamical behavior for the latter cannot be ascribed to the charge dispersal in the TBPE anion. Since aromatic amines do not react with GH to from G^- in the usual conditions, the basicity of amines must be correlated to this reaction. However, it is rather critical to say that the thermodynamical data are correlated to the pK_a-values of the amines in water. This could be ascribed to the leveling effect in acetonitrile. There seem to exist an approximate linear free energy relationship. However, the plot of $\Delta H°$ against $\Delta S°$ was found to scatter considerably and so, much cannot be said for this.

Opposing Reactions between GH and Primary Amines. In the foregoing section, we suggested a side reaction of GH with primary amines to form a substance with λ_{max} near 240 nm. Inspection of Fig. 4 shows that there may be contributions of more than one species to the absorption band over a range of 250—300 nm. The absorption spectrum for GH_3 has band maxima at 237 (sharp) and 276 nm, while GH has a band maximum at 263 nm in the UV region. A proper mixture of GH and GH_3 reproduced a spectrum similar to that of the solution after equilibrium. Hence we can conclude that this solution contains a substance, for which the canonical electronic structures are similar to that of GH_3. Therefore, we propose the following reversible reaction scheme:

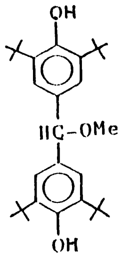


$$\mathrm{GH} + \mathrm{Amines} \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \mathrm{G}^- + \mathrm{AmH}^+ \quad \xrightarrow{\text{slow}} \mathrm{X} \qquad (6)$$

Unfortunately, the isolation of X has been unsuccessful. However, when an excess amount of acetic acid over amine was added to the solution, the peak at 580 nm disappeared at once, and then the peak at 396 nm due to GH increased gradually at the expense of the peak at 240 nm to reach a maximum. From the intensity at 396 nm, GH was found to be restored quantitatively. Thus, the skeleton of GH must have been kept unbroken in X. From the above findings, we propose the following structure for X.



X



GMeO

This structure may be electronically similar to that of GH_3. Further, the electronic spectrum in the UV region of the compound GMeO[4] (see above) was also inspected. The spectral data in the near UV region for relevant compounds are given in Table 4. Mutual comparison of these data shows almost undoubtedly that X has the structure given above.

Why the above reaction does not occur for secondary and tertiary amines? This could reasonably be explained in terms of steric hindrance. The -CH= group in GH is blocked by the two phenyl groups and this would make the nucleophilic attact of the amino nitrogen of these types of compounds on this carbon difficult. This idea is justified by the fact that *t*-butylamine for which the amino nitrogen is surrounded by the bulky methyl groups, did not react at all.

Table 4. Comparison of Spectra in the Near UV Region

Compound	λ_{max}/nm			
GH		263		280—290 (sh)
GH_3	237		276	282—288 (sh)
$GH+GH_3$	237	268		280—288 (sh)
Product[a]	238	270		278—286 (sh)
GMeO	238		272—278 (sh)	283

a) Spectrum of a mixture of GH and hexylamine taken after a long time.

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