

A STUDY OF SPECIFIC AND NON-SPECIFIC INTERACTIONS OF EPOXY GROUP OF 1,2-EPOXYBUTANE IN SOLUTIONS

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IR spectra have been measured of tetrachloromethane solutions of 1,2-epoxybutane with nine substituted phenols at 25 and 60°C in the range 3700 to 3200 cm^{-1} and of solutions of 1,2-epoxybutane in 21 solvents and in gas phase in the range 4600–4500 cm^{-1} . Thermodynamic functions have been computed for association of the phenols with 1,2-epoxybutane. The band position of the combination frequency, in the range 4540 cm^{-1} has been correlated with dielectric constants and refractive indices of the solvents with the use of the Buckingham equation.

Epoxy group forms a strong hydrogen bonding with hydroxyl hydrogen atom of phenols. Formation of this bonding is considered to be the first step of curing process of epoxy resins in the cases in which phenols are used as curing accelerators¹. IR spectroscopy turned out to be a suitable method for a study of interactions in solutions for both the cases of so called specific interactions leading to formation of stable complexes (*e.g.* on the basis of hydrogen bond) and so called non-specific interactions in solutions giving collision complexes of short life-time².

The aim of this work was to find thermodynamic parameters of formation of hydrogen bond between 1,2-epoxybutane and substituted phenols and study the influence of medium on the band position of combination frequency of a terminal epoxy group³.

EXPERIMENTAL

The used phenols were purified by distillation and were kept over P_2O_5 . 1,2-Epoxybutane (Merck) was used without further modifications. The used solvents were dried, rectified and kept over molecular sieves. The ternary mixtures of 1,2-epoxybutane, phenol and CCl_4 were studied in 1.5 cm cells, the solution temperature being maintained within $\pm 0.5^\circ\text{C}$. Spectrum of gaseous 1,2-epoxybutane was measured in a 10 cm cell. IR spectra were measured with a Zeiss UR-20 spectrophotometer (Jena).

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RESULTS AND DISCUSSION

Table I gives equilibrium constants and enthalpies of association of substituted phenols with 1,2-epoxybutane in CCl_4 , Table II gives the wave number values of the combination band of the terminal epoxy group found in 21 solvents and in gas phase. The values given represent arithmetic mean of three measurements each. The association equilibrium constants of the substituted phenols with epoxide were within the ranges 3.6 to 31.8 m^3/kmol and 1.6 to 13.4 m^3/kmol at 25 and 60°C, respectively, and they depended on the nature of the substituent. The association enthalpies also depended on the substituent nature, being within the range -3.6 to -15.0 kJ/mol for the set measured. In accordance with the linear free energy relationship, the logarithms of the equilibrium constants depend linearly on the Hammett substituent constants of the ring substituents. This dependence was found graphically to have the following form for the studied set of phenols: $\log K_{25} = 0.81 + 1.04\sigma$ and $\log K_{60} = 0.52 + 0.83\sigma$. Compared with other electron-donor solvents⁴ the found thermodynamic constants indicate that the proton-acceptor ability of 1,2-epoxybutane for formation of a hydrogen bond with phenols is comparable with those of 1,4-dioxane and acetonitrile.

Influence of solvent on position of the band of combination frequency of terminal epoxy group was evaluated with the use of the Buckingham equation⁵ which has the following form for the set studied:

$$\nu (\text{cm}^{-1}) = 4532.0 + 52.1(\epsilon - 1)/(2\epsilon + 1) - 108.4(n^2 - 1)/(2n^2 + 1).$$

TABLE I

Equilibrium Constants and Enthalpies of Formation of Complexes between Substituted Phenols and 1,2-Epoxybutane in CCl_4

Substituent	σ^a	K_{25} m^3/kmol	ΔH kJ/mol
4-OC ₂ H ₅	-0.25	3.6	- 3.6
4-CH ₃	-0.15	4.5	- 5.8
3-CH ₃	-0.10	6.0	- 7.1
-H	0.00	6.6	- 9.2
4-Br	0.23	9.4	- 7.1
3-Cl	0.38	17.1	- 9.6
3-Br	0.39	16.0	-10.9
3-CN	0.61	28.6	- 9.2
3-NO ₂	0.70	31.8	-15.0

^a The substituent constants were taken from ref.⁷.

TABLE II
Influence of Solvent on Combination Frequency of Terminal Epoxy Group of 1,2-Epoxybutane (cm^{-1})^a

Solvent	$(\epsilon - 1)/(2\epsilon + 1)$	$(n^2 - 1)/(2n^2 + 1)$	ν	Difference between the calculated and the found values
Gas phase	0.0000	0.0000	4 532	0.0
n-Hexane	0.1853	0.1853	4 523	-1.5
Cyclohexane	0.2018	0.2038	4 522	-1.6
Tetrachloromethane	0.2251	0.2142	4 524	-3.5
Benzene	0.2296	0.2267	4 524	-4.7
Toluene	0.2395	0.2341	4 525	-5.9
Carbon disulphide	0.2603	0.2610	4 513	4.2
Bromoform	0.3449	0.2536	4 523	-0.6
Dibutyl ether	0.2893	0.1940	4 523	3.0
Chloroform	0.3563	0.2094	4 532	-4.2
Diiodomethane	0.3710	0.2869	4 518	2.2
Chlorobenzene	0.3775	0.2337	4 525	1.3
Iodomethane	0.3981	0.2356	4 528	-0.9
Tetrahydrofuran	0.4037	0.1971	4 529	2.6
Tetrachloroethane	0.4138	0.2248	4 532	-2.9
Dichloromethane	0.4202	0.2024	4 535	-3.1
Pyridine	0.4414	0.2292	4 526	4.1
Acetophenone	0.4581	0.2366	4 530	0.2
Acetone	0.4682	0.1804	4 538	-1.2
Nitrobenzene	0.4788	0.2418	4 532	-1.3
Acetonitrile	0.4796	0.1740	4 539	-0.9
Nitromethane	0.4798	0.1879	4 538	-1.4

^a The terms containing ϵ and n^2 were taken from ref.⁶.

The correlation coefficient was 0.913. From the equation it can be seen that the absolute term agrees with the wave number found in gas phase (4532 cm^{-1}) where the epoxybutane molecules are not affected by any other component. As compared with majority of the systems measured up to now it is interesting that the parameter characterizing the effect of dielectric constant on the studied absorption band position has a positive value.

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