

## Note

### Study of interactions of tri-*n*-alkylamines with 3,5-dinitrophenol by means of gas-liquid chromatography

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The use of gas-liquid chromatography (GLC) for the study of electron donor-acceptor interactions and hydrogen-bonded adducts has been the subject of numerous recent papers<sup>1-6</sup>. The topic has been comprehensively reviewed. Interpretation of the results at first led to considerable confusion, but important advances in the treatment of these data have been made during the past ten years. GLC can now be regarded as a complementary method to spectroscopic techniques for the study of problems associated with complexing phenomena.

The interactions of trialkylamines with different substituted phenols and other acids has been studied by several authors<sup>8,9</sup> with different spectroscopic techniques, but not with GLC. In this paper we describe the use of GLC for such a system. The interactions of tri-*n*-alkylamines (from trimethyl- to tributyl-amine) with 3,5-dinitrophenol were studied.

#### THEORETICAL

We used the approach of Eon *et al.*<sup>3</sup>. For the case of a volatile solute B, eluted through a column containing a non-volatile complexing agent A mixed with an inert solvent S, the equilibrium constant for AB complex formation is given by eqn. 1:

$$K_R V_{AS}^{\circ} = K_R^{\circ} V_S^{\circ} [1 + (\psi + K^x) X_A] \quad (1)$$

$$\psi = \frac{V_A^{\circ}}{V_S^{\circ}} \frac{\exp(V_B^{\circ}/V_A^{\circ})}{\exp(V_B^{\circ}/V_S^{\circ})} - 1$$

where  $K_R^{\circ}$  is the partition coefficient of B on the pure inert solvent,  $V_S^{\circ}$ ,  $V_A^{\circ}$  and  $V_B^{\circ}$  are molar volumes of pure S, A and B,  $V_{AS}^{\circ}$  is the molar volume of the mixture A-S of molar fraction  $X_A$ , and  $K^x$  is thermodynamic equilibrium constant defined as:

$$K^x = \frac{X_{AB}}{X_A \cdot X_B} \frac{\gamma_{AB}^x}{\gamma_A^x \gamma_B^x} \quad (2)$$

where  $\gamma_i^*$  is the activity coefficient of the species  $i$  in the pure solvent  $S$ , the reference state for the chemical potentials being the infinitely dilute solution.

In our case solute  $B$  refers to the amine, agent  $A$  to 3,5-dinitrophenol, and solvent  $S$  to benzyldiphenyl.

Extensive studies of carboxylic acid-amine complexes in aprotic solvents have revealed the presence of several competing equilibria<sup>8,9</sup>, but for the system used in this work 1:1 complex formation between amine and phenol can be assumed. 3,5-Dinitrophenol, which has no *ortho*-substituents, thus contains no intramolecular hydrogen bonds; the low concentrations used prevented self-association of phenol or amine. Enthalpy and entropy values were calculated according to well-known principles<sup>5-10</sup> from the equilibrium constants obtained from eqn. 1.

## EXPERIMENTAL

Measurements were performed on a Chromacon 9580 gas chromatograph equipped with a thermal conductivity detector. Glass columns (80 cm  $\times$  0.40 cm I.D.) were used, loaded with 25% of liquid phase on Chromosorb W A/W, 80-100 mesh. The liquid phase was weighed and dissolved in chloroform; the support was mixed with this solution and the solvent evaporated under flowing air. The exact amount of the stationary phase was determined by the combustion method. Five different stationary phases were used with a 3,5-dinitrophenol molar fraction ranging from 0 to 0.28. The column temperature, measured with an iron-constantan thermocouple, was 100°, 110° or 115°, constant to within  $\pm 0.2^\circ$ . High-purity nitrogen was used as the carrier gas. The sample sizes were between 0.05 and 0.1  $\mu$ l. Within this range, we found no dependence of the retention time on the amount of sample.

The stationary phase was benzyldiphenyl (May & Baker, Dagenham, Great Britain) purified by double crystallization from methanol. 3,5-Dinitrophenol was prepared by the methods of Holleman and Wilhelmy<sup>11</sup> and Lobry de Bruyn<sup>12</sup> and by demethylation<sup>13</sup> of 3,5-dinitroanisole. The final product was obtained<sup>14</sup> by double crystallization from benzene-pentane, and its identity and purity were checked from its infrared spectrum and melting point (124.5-125°). The solutes were purified by vacuum distillation, although high purity is not necessary for such work. Optical measurements, made with a Cary 16 spectrophotometer, covered the range 180-800 nm with an accuracy of 0.5 nm and absorbance measurements to 0.0007 absorbance unit at 0.5 absorbance. The optical data were evaluated via the Scott<sup>15</sup> variant of the Benesi-Hildebrand equation.

## RESULTS AND DISCUSSION

The values of  $K^* + \psi$  obtained from eqn. 1 by least-squares treatment of the experimental data are in Table I, together with calculated  $\psi$  values and values of  $K^*$ .

The enthalpy and entropy values are in Table II, together with spectrophotometric values obtained from different sources. The correlation coefficients were in all cases high, justifying the relations used.

The agreement between GLC and spectrophotometric data in Table II is very good. In spite of the different solvents and temperatures used in the two methods, the

TABLE I

GLC PARAMETERS OF COMPLEX FORMATION OF 3,5-DINITROPHENOL WITH AMINES

Compound	T(°C)	K <sup>x</sup> + $\psi$	$\psi$	K <sup>x</sup>	ln K <sup>x</sup>
Trimethylamine	100	19.79	-0.079	19.71	2.98
	110	14.83	-0.066	14.76	2.69
	115	12.19	-0.060	12.13	2.50
Triethylamine	100	12.68	0.033	12.71	2.54
	110	9.45	0.043	9.49	2.25
	115	8.05	0.048	8.10	2.09
Tri-n-propylamine	100	8.17	0.311	8.48	2.14
	110	5.48	0.327	5.81	1.76
	115	4.88	0.333	5.21	1.65
Tri-n-butylamine	100	13.93	0.631	14.56	2.68
	110	10.28	0.647	10.93	2.39
	115	9.24	0.657	9.90	2.29

two sets of data show smaller discrepancies than are often seen in the application of different spectroscopic methods to the same system.

GLC can thus be successfully applied to the study of complexing phenomena of aliphatic amines and substituted phenols.

TABLE II

THERMODYNAMIC PARAMETERS OF COMPLEX FORMATION OF 3,5-DINITROPHENOL WITH AMINES

Methods: (a) values obtained from GLC measurements in this work, with benzyldiphenyl as solvent; (b) spectroscopic values at 25° for complex formation of 3,5-dinitrophenol with amines in benzene; (c) spectroscopic values at 25° for complex formation of 3,4-dinitrophenol with amines in benzene<sup>10</sup>. The reference state for the chemical potentials is the infinitely dilute solution in all three cases.

Compound	Method	- $\Delta H^\circ$ (kcal/mol)	- $\Delta G^\circ$ (kcal/mol)	- $\Delta S^\circ$ (cal/deg)
Trimethylamine	a	9.083	—	—
	b	—	—	—
	c	—	—	—
Triethylamine	a	8.621	—	—
	b	7.52 ± 0.04	4.14 ± 0.06	11.40 ± 0.14
	c	8.1 ± 1.7	4.77 ± 0.11	11.1 ± 5.9
Tri-n-propylamine	a	10.138	—	—
	b	8.28 ± 0.81	—	16.89 ± 0.27
	c	9.2 ± 1.3	3.89 ± 0.04	17.7 ± 4.4
Tri-n-butylamine	a	7.955	—	—
	b	7.69 ± 0.02	3.39 ± 0.03	14.40 ± 0.6
	c	10.3 ± 0.2	3.98 ± 0.01	21.2 ± 0.6

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