Determination of Stability Constants by Gas–Liquid Chromatography for the π-Complexing of Aromatic Solvents and Monomers with a Nitroxide Radical

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Summary Stability constants have been determined by g.l.c. for the π-complexing of aromatic solvents and monomers with the t-butyl mesityl nitroxide radical over the temperature range 50—85°.

GAS CHROMATOGRAPHY has been used to determine stability constants (K_C) for a number of different kinds of equilibria. We have applied this technique to the solvent and monomer (X) interaction with a nitroxide radical (R·) over the temperature range 50—85°. We assume that a 1 : 1 complex is formed.

$$\mathrm{R\cdot} + \mathrm{X} \xrightleftharpoons{K_C} \mathrm{RX\cdot}$$

R· = t-butyl mesityl nitroxide;

X = benzene, chlorobenzene, bromobenzene; styrene, methyl methacrylate, methacrylonitrile, and methyl acrylate.

The apparent gas-chromatographic partition coefficient K_R is given by equation (A), where C_R is the concentration of the radical R, K_{R^0} is

$$K_R = K_{R^0}(1 + K_C C_R) \qquad \text{(A)}$$

the partition coefficient of X between the gas-chromatographic solvent squalane and the gas phase [equation (B)]. The retention volume for

$$X_{(g)} \rightleftarrows X_{(l)} \qquad K_{R^0} \qquad \text{(B)}$$

$X(V_R)$ is related to K_{R^0} by equation (C), where V_L is the total

$$V_R = K_{R^0}\, V_L \qquad \text{(C)}$$

volume of squalane on the column. When $C_R = 0$, $K_R = K_{R^0}$ and hence we may find K_C from equation (D).

$$\frac{V_R}{V_{R^0}} = 1 + K_C C_R \qquad \text{(D)}$$

The apparatus was a Perkin Elmer G.L.C. employing a hydrogen flame ionisation detector, N_2 carrier gas, and 50 m capillary columns containing either squalane, or a solution of R· in squalane. 1 μl of a 0·5% acetone solution of the solvents or monomers together with inert markers cyclohexane and n-nonane, was injected into a column *via* an

Thermodynamic data for π-complexation with t-butyl mesityl nitroxide at 60°

Solvent or monomer (X)	$-\ln K_C$	$-\Delta H^\circ$ kcal. mole^{-1a}	$-\Delta S^\circ$ Cal. mole^{-1} deg^{-1a}	ΔG° kcal. mole^{-1a}
Benzene	3·12	5·8	23·6	2·1
Chlorobenzene	2·36	3·5	15·2	1·6
Bromobenzene	1·94	2·2	10·5	1·3
Styrene	2·12	1·5	8·7	1·4
Methyl methacrylate ..	2·44	4·4	18·1	1·6
Methyl acrylate	2·70	10·9	38·1	1·7
Methacrylonitrile ..	3·15	7·1	27·6	2·1

[a] 1 cal. = 4·184 J.

injection block heated to 200° and a stream splitter which reduced the volume finally going on to the column by two powers of ten.

The solution of equation (D) for K_C at various temperatures led to the usual thermodynamic parameters given in the Table. The bond energy of complex formation lies in the range 2—11 kcal mole^{-1}. This range is in accord with the value of 6·2 kcal mole^{-1} obtained by Buchachenko *et al.*[2] for the complexation of dianisyl nitroxide with benzene by other methods. In addition, this value is not far removed from the value obtained by us for benzene and t-butyl mesityl nitroxide, of 5·8 kcal mole^{-1}.

These results have some significance in connection with different rates of polymerisation as a function of solvent.

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[1] See: D. F. Cadogan and J. H. Purnell, *J. Chem. Soc.* (*A*), 1968, 2133.

[2] A. L. Buchachenko, O. P. Sukhanova, L. A. Kalashnikova, and M. B. Neiman, *Kinetika i Kataliz*, 1965, **6**, 601; L. A. Kalashnikova, M. B. Neiman, and A. L. Buchachenko, *Russ. J. Phys. Chem.*, 1968, **42**, 598; L. A. Kalashnikova, A. L. Buchachenko, M. B. Neiman, and E. G. Rozantsev, *ibid.*, 1969, **43**, 31.