

Note

Formation constants and activity coefficients from gas-liquid chromatographic measurements

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The complexation of silver ions with olefins is well known^{1,2} and the formation constants of many olefins with silver ions have been measured³⁻⁶. As cyclopropane and other compounds containing bent sigma bonds have shown "pseudo-conjugated" properties^{7,8} it seemed possible that silver ions would react with these compounds in much the same way as silver ions react with olefins.

In this work gas-liquid chromatography has again been used to determine formation constants for hex-1-ene and cyclohexene with silver ions. Furthermore it has been used to investigate the interactions of three cyclopropane containing compounds (cyclopropane, *cis,anti,cis*-tricyclo[3.1.0.0^{2,4}]hexane and tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane; see Fig. 1) with silver ions.



Fig. 1. Structures of (a) *cis,anti,cis*-tricyclo[3.1.0.0^{2,4}]hexane and (b) tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane.

EXPERIMENTAL

Equipment

A Shandon gas chromatograph was used with a sensitive catharometer detector and recorder. The instrument was modified so that the column temperature could be kept constant to within ± 0.01 °K⁹. A mercury manometer was used to determine the helium inlet pressures and a soap bubble flow meter¹⁰ in conjunction with an electronic timer was used to measure the helium carrier gas flow-rate. The precision of the flow meter was estimated at better than $\pm 0.2\%$. The flow-rates used in the experiments ranged between 0.4 cm³/sec and 1.1 cm³/sec. No appreciable difference in partition coefficients with different flow-rate was observed.

Column

Silver nitrate and sodium nitrate (eliminate the salting-out effect) were dissolved in ethylene glycol and made up to 50 cm³. The densities of these solutions were

determined at 298.15 °K and 314.00 °K. The five column packings were each carefully made by weighing and shaking a small amount of the above solutions with Anakrom 545A (110–120 mesh) (Analabs, North Haven, Conn., U.S.A.). The solvent loadings on the five columns ranged from 28% to 33%. Earlier attempts at using Celite (BDH, Poole, Great Britain) as a solid support failed because the Celite turned grey on adding the silver nitrate solution. This grey colour also formed when the addition was done in the dark and is most likely due to impurities in the Celite partially reducing the silver ions to the metal.

The columns were prepared in 4.3-mm-bore stainless-steel tubing, each 2 m in length.

Operating conditions

The sample size of the injected liquid was always smaller than 0.3 μ l and was usually 0.1 μ l. No difference in retention times was noticed with different sample in this range. The injected volume of the gas samples, including air which was used to measure the hold-up time, was always less than 20 μ l.

The peaks obtained were virtually symmetrical. The retention times were determined from peak maximum times¹⁰. The column outlet pressure was taken as atmospheric pressure.

Materials

Hex-1-ene (BHD), cyclohexane (Merck, Darmstadt, G.F.R.), cyclohexene (Merck) and cyclopropane (Afrox, Johannesburg, South Africa) were used without purification. The tricyclohexane was made using the method of Closs and Krantz¹¹ and Schipperijn and Lukas¹² and was used after repeated distillation. The tetracycloheptane was obtained by photolysing bicyclo[2.2.1]hepta-2,5-diene¹³ followed by distillation.

RESULTS AND DISCUSSION

The partition coefficients, $K_1(0)$ and K_1 were calculated using the method of Muhs and Weiss³ and are tabulated in Table I. The formation constants, K_F , again calculated using the method of Muhs and Weiss³, are given in Table II.

The values of K_F , K_1 and $K_1(0)$ are estimated to be reproducible to $\pm 3\%$. The formation constants at 30.85 °C for hex-1-ene and cyclohexene compare very well with the results of refs. 3–6, although they have been obtained at other temperatures.

The formation constant for the cyclohexane–silver ion “complex” is zero as expected; the formation constants for “interactions” of the silver ion with cyclopropane, tricyclohexane and tetracycloheptane were also found to be zero. The strained three-membered ring compounds did not react with the silver ions on the column to form rearranged species as might have been predicted⁴. Had such a reaction taken place the partition coefficients calculated from the silver-impregnated columns would surely have been different from the partition coefficient calculated from columns containing no silver ions. This effect in cyclopropane and spiro-pentane has, however, been reported by Shabtai *et al.*¹⁵.

Assuming that the thermodynamic equilibrium constants vary with temperature in the same way as the formation constants, we have estimated ΔH° (in the

TABLE I

THE CONCENTRATION OF SILVER NITRATE [Ag⁺] AND SODIUM NITRATE [Na⁺] ON THE COLUMNS AND THE PARTITION COEFFICIENTS AT 298.15° K AND 314.00° K

	Column				
	1	2	3	4	5
[Ag ⁺] (M)	0.000	0.227	0.407	0.599	0.854
[Na ⁺] (M)	0.821	0.615	0.419	0.233	0.000
298.15° K	<i>K</i> ₁ (0)	<i>K</i> ₁			
Cyclopropane	1.05	1.00	0.98	1.04	1.03
<i>n</i> -Hex-1-ene	4.92	13.15	20.46	28.93	36.71
Cyclohexane	9.82	9.74	9.63	9.85	9.68
Cyclohexene	21.33	58.9	92.2	119.5	161.9
Tricyclohexane	21.00	21.13	21.32	21.07	20.98
Tetracycloheptane	122.8	120.3	118.6	121.5	122.6
314.00° K	<i>K</i> ₁ (0)	<i>K</i> ₁			
Cyclopropane	—	—	—	—	—
<i>n</i> -Hex-1-ene	3.63	7.22	10.15	12.98	17.50
Cyclohexane	6.03	6.19	6.05	6.17	6.18
Cyclohexene	15.60	25.23	34.33	45.11	56.96
Tricyclohexane	14.15	14.46	14.21	14.35	14.23
Tetracycloheptane	—	—	—	—	—

TABLE II

FORMATION CONSTANTS, *K*_F, VAPOUR PRESSURES, *P*₁ AND INFINITE DILUTE ACTIVITY COEFFICIENTS, γ_{13} AT 298.15° K AND 314.00° K

Solute	<i>K</i> _F		<i>P</i> ₁ (torr)		γ_{13}	
	298.15° K	314.00° K	298.15° K	314.00° K	298.15° K	314.00° K
Cyclohexane	0	0	97.61	191.14	348	301
Cyclohexene	7.40	3.31	88.32	175.41	180	126
Tricyclohexane	0	0	149.79	278.85	106	88
Tetracycloheptane	0	—	—	—	—	—

temperature range 298 °K to 314 °K) for silver ion complexes with hex-1-ene and cyclohexane to be -26 kJ/mol and -40 kJ/mol respectively.

The activity coefficients, γ_{13} for the hydrocarbon solutes in ethylene glycol have been calculated from the partition coefficient *K*₁(0) of Table I and the vapour pressures of Table II using the equation¹⁰:

$$V_N = K_1(0)V_3 = n_3RT/(\gamma_{13}^\infty P_1^0)$$

where *V*_N is the net retention volume, *V*₃ the solvent volume, *n*₃ the amount of solvent ethylene glycol on the column and *P*₁⁰ the vapour pressure of the solute at temperature *T*. The amount of ethylene glycol on column 1 was 0.0497 mol.

The values of γ_{13} are estimated to be reproducible to ±6% and are tabulated in Table II.

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