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GAS CHROMATOGRAPHIC DETERMINATION OF EQUILIBRIUM CONSTANTS FOR EXCHANGE REACTIONS

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SUMMARY

A gas–liquid chromatographic method is described for the determination of the equilibrium constants of exchange reactions of the type $A + BC \rightleftharpoons AB + C$, which occur in a liquid phase between an eluted substance A and a non-volatile substance BC that is dissolved in a stationary liquid, provided that the products of the reaction of AB and C also have very low volatilities. The equilibrium constant can be estimated from the intercept of the linear graph of retention volumes corresponding to the maxima of asymmetrical peaks plotted against the reciprocal of the square roots of their heights.

By this procedure, the equilibrium constants for the displacement of cyclooctene by 1,3-butadiene and 1-butene from acetylacetonatocarbonylcyclooctenerhodium(I) in *n*-dodecane solution were determined.

INTRODUCTION

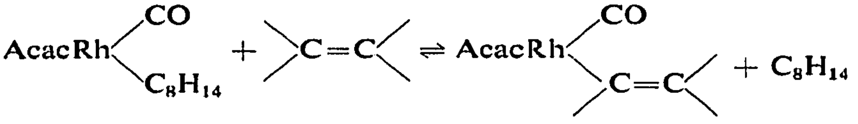
Gas–liquid chromatography (GLC) has been used successfully for investigating reversible addition reactions when a substance passing through a column interacts with a stationary phase component to give a dissociable complex[1–5].

In this paper, the possibilities of using GLC for the investigation of exchange reactions of the type

$$A + BC \overset{K_p}{\rightleftharpoons} AB + C \tag{1}$$

which occur in a liquid phase between a component BC and an eluted substance A are discussed.

The simplest most widely encountered case for the mathematical treatment of chromatographic processes is the case when substances BC, AB and C have such low volatilities under the experimental conditions used that their concentrations in the gas phase, and hence their velocities of movement along the chromatographic column compared with those of substance A, can be neglected. In this case, at every position in the column an equilibrium will be established in the liquid phase at sufficiently high rates of the forward and reverse reactions. Reactions of the type in eqn. 1 occur widely and include the exchange and displacement of ligands in transition metal complexes. One of these reactions, the displacement of cyclooctene by other unsaturated hydrocarbons from acetylacetonatocarbonylcyclooctenerhodium(I) in a hydrocarbon solution was the subject of our present investigation:



(BC) (A) (AB) (C) (2)

THEORETICAL

In cases when the kinetic factors can be neglected, the rate at which the zone of a sufficiently low constant concentration of an eluted substance moves along the column and the retention volume of this zone, $V_R(c)$, are usually determined by the derivative of the isotherm $q = \mathrm{f}(c)$ of the distribution of the eluted substance between the liquid and gas phases with respect to the concentration of the substance in the gas phase, c (ref. 7):

$$V_R^0(c) = V_L \cdot \frac{\mathrm{d}q}{\mathrm{d}c} = V_L\, K(c) \tag{3}$$

where $V_R^0(c)$ is the corrected reduced retention volume and V_L is the volume of the liquid phase in the column.

Thus, in the case under consideration, with reaction 1 taking place in the liquid phase of the column, it is necessary to derive an expression for $\mathrm{d}q_\mathrm{A}/\mathrm{d}c_\mathrm{A} = K(c_\mathrm{A})$ for the eluted substance A.

It is known that in the general case

$$q_\mathrm{A} = \sum_i \sum_j \ldots \sum_n i\,[\mathrm{A}_i\,\mathrm{B}_j\,\ldots\,\mathrm{F}_n] \tag{4}$$

where $[\mathrm{A}_i\mathrm{B}_j\ldots\mathrm{F}_n]$ are the equilibrium concentrations of the substance having the composition $\mathrm{A}_i\mathrm{B}_j\ldots\mathrm{F}_n$ in the liquid phase.

In this case

$$q_\mathrm{A} = [\mathrm{A}] + [\mathrm{AB}] \tag{5}$$

The concentration [AB] can be determined from the expression for the equilibrium constant of reaction 1:

$$K_p = \frac{[\mathrm{AB}]\,[\mathrm{C}]}{[\mathrm{A}]\,[\mathrm{BC}]} \cdot \frac{\gamma_\mathrm{AB} \cdot \gamma_\mathrm{C}}{\gamma_\mathrm{A} \cdot \gamma_\mathrm{BC}} \tag{6}$$

or

$$K_p \cdot \mathrm{f}(\gamma) = \frac{[\mathrm{AB}]\,[\mathrm{C}]}{[\mathrm{A}]\,[\mathrm{BC}]} \tag{7}$$

where

$$\mathrm{f}(\gamma) = \frac{\gamma_\mathrm{A} \cdot \gamma_\mathrm{BC}}{\gamma_\mathrm{AB} \cdot \gamma_\mathrm{C}}$$

Taking into consideration a sufficiently low concentration of substance BC in the stationary phase and the fact that under gas chromatographic conditions the volume of the eluted substance A is also small, it can be assumed (taking a state of infinite dilution in a hyhrocarbon solvent as standard states for substances A, BC, AB and C) that the activity coefficients for these substances, γ_i, under the conditions used in chromatographic investigations, are close to unity and, hence, $f(\gamma) \approx 1$. Then, eqn. 7 can be written as

$$K_p = \frac{[\mathrm{AB}]\,[\mathrm{C}]}{[\mathrm{A}]\,[\mathrm{BC}]} = \frac{[\mathrm{AB}]^2}{[\mathrm{A}]\,(a - [\mathrm{AB}])} \tag{8}$$

where a is the initial concentration of substance BC in the liquid phase.

Hence

$$[\mathrm{AB}] = -\tfrac{1}{2} K_p\,[\mathrm{A}] \left(1 - \sqrt{1 + \frac{4a}{K_p\,[\mathrm{A}]}}\right) \tag{9}$$

Substituting eqn. 9 into eqn. 5 and differentiating q_A with respect to c_A, we obtain

$$\begin{aligned} K(c) &= \frac{\mathrm{d}q_\mathrm{A}}{\mathrm{d}c_\mathrm{A}} = \frac{\mathrm{d}q_\mathrm{A}}{\mathrm{d}\,[\mathrm{A}]} \cdot \frac{\mathrm{d}\,[\mathrm{A}]}{\mathrm{d}c_\mathrm{A}} = K_0 \cdot \frac{\mathrm{d}q_\mathrm{A}}{\mathrm{d}\,[\mathrm{A}]} = \\ &= K_0 \left(1 - \tfrac{1}{2} K_p + \tfrac{1}{2} K_p^{\frac{1}{2}}\,[\mathrm{A}]^{-\frac{1}{2}} \cdot \frac{K_p\,[\mathrm{A}] + 2a}{\sqrt{K_p\,[\mathrm{A}] + 4a}}\right) \end{aligned} \tag{10}$$

where

$$K_0 = \frac{\mathrm{d}\,[\mathrm{A}]}{\mathrm{d}c_\mathrm{A}} = \frac{[\mathrm{A}]}{c_\mathrm{A}} \tag{11}$$

i.e., K_0 is the partition coefficient of substance A molecules between the liquid and gas phases; in this case, it is assumed that at sufficiently low values of a, K_0 is equal to the partition coefficient in a pure solvent and is independent of the sample size.

Taking eqn. 11 into account, it is possible to express $K(c)$ in terms of the concentration of the substance in the gas phase, c_A, recorded as a chromatogram at the end of the column:

$$K(c) = K_0 - \tfrac{1}{2} K_0\,K_p + \tfrac{1}{2} K_p^{\frac{1}{2}}\,K_0^{\frac{1}{2}}\,c_\mathrm{A}^{-\frac{1}{2}} \cdot \frac{K_p\,K_0\,c_\mathrm{A} + 2a}{\sqrt{K_p\,K_0\,c_\mathrm{A} + 4a}} \tag{12}$$

or

$$K(h) = K_0 - \tfrac{1}{2} K_0\,K_p + \tfrac{1}{2} \cdot \frac{K_p^{\frac{1}{2}}\,K_0^{\frac{1}{2}}}{\kappa^{\frac{1}{2}}\,h^{\frac{1}{2}}} \cdot \frac{K_p\,K_0\,\kappa h + 2a}{\sqrt{K_p\,K_0\,\kappa h + 4a}} \tag{13}$$

where h is the recorder deflection from the base-line and κ is the detector constant for a given substance determined by the method described earlier[8].

Thus, from eqns. 3 and 13, it follows that if a reaction of the type in eqn. 1 occurs in a chromatographic column, the chromatographic peaks of substance A should be sharply asymmetrical and will be characterized by a vertical leading edge and a diffused tail. At sufficiently low concentrations of substance A, *i.e.*, when $K_p K_0 \kappa h \ll a$, a linear dependence of $K(h)$ upon $1/\sqrt{h}$ is obtained.

$$K(h) = K_0 - \tfrac{1}{2} K_0\,K_p + \tfrac{1}{2} \left(\frac{K_p\,K_0\,a}{\kappa}\right)^{\frac{1}{2}} \cdot \frac{1}{\sqrt{h}} \tag{14}$$

Extrapolating this relationship to a value of zero for $1/\sqrt{h}$, we obtain an intercept on the ordinate of $K_0 - {}^1/_2 K_0 K_p$, which can be easily used for the determination of the equilibrium constant, K_p.

With increase in h, the values of $K(h)$ and hence of V_R^0 of the corresponding concentration decrease, in the limit approaching the K_0 or V_R^0 values for a pure solvent.

EXPERIMENTAL

As the stationary phase, solutions of acetylacetonatocarbonylcyclooctenerhodium(I) (BC) in *n*-dodecane and *n*-pentadecane were used. BC was obtained by refluxing an excess of cyclooctene with acetylacetonatodicarbonylrhodium(I) (synthesized by the procedure described by Varshavskii and Cherkasova[9]) in benzene. The compound was recrystallized from a mixture of ethanol and diethyl ether.

Preliminary tests showed that the reproducibility of results was impaired if the preparation of the column packing and the filling of the column were performed in air. In order to avoid this, the following procedure was developed.

A definite volume (1–2 ml) of a hydrocarbon solution (0.005–0.05 M) of substance BC was added directly, under dry argon, to 7.5 g of Celite-545, pre-treated in a vacuum at 150° for 3 h. Homogenization of the packing in a hermetically sealed vessel under argon was carried out for 3 h using a shaker. A helical glass chromatographic column (1 m × 4 mm I.D.) was filled under argon and placed in a column oven controlled to within ± 0.05°. High-purity helium was used as the carrier gas. A thermal conductivity cell was employed as detector. Experiments were conducted in the temperature range 10–30°.

The calculation of retention volumes from the chromatograms was performed by a standard procedure.

A study was made of the displacement of cyclooctene from substance BC by 1-butene, 1,3-butadiene and by some unsaturated C_5 hydrocarbons according to eqn. 2. Under the experimental conditions, the velocity of the movement of cyclooctene along the chromatographic column was 2–3 orders of magnitude lower than that of eluted C_4 and C_5 hydrocarbons. Thus, the main condition for the establishment of equilibrium in the liquid phase was fulfilled (substances BC and A undoubtedly had extremely low volatilities).

RESULTS AND DISCUSSION

The peaks for the unsaturated hydrocarbons were very asymmetrical. Fig. 1 shows the chromatograms of 1,3-butadiene obtained with a column containing the BC solution ($a = 0.02$ M), the samples being of different sizes. In contrast, the chromatogram of *n*-butane shows a symmetrical peak, its retention time being independent of the size of the sample.

The merging of the rear edges of the peaks with increasing time to form a single curve and the almost vertical positions of the initial edges of the peaks indicate that in this particular case the kinetic factors have little influence on the formation of a chromatographic peak, as already reported, for example, by Kiselev and Yashin[10]. However, with small peaks that had a long retention time, an appreciable deviation of

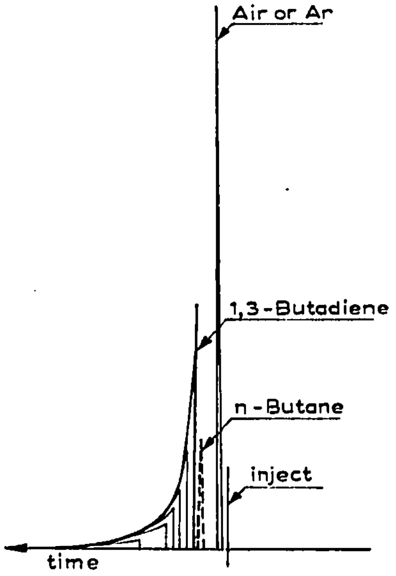


Fig. 1. Superimposed chromatograms of 1,3-butadiene samples of different sizes. Stationary phase: solution of (acac)Rh(CO)(C_8H_{14}) in *n*-dodecane ($a = 0.02$ *M*). Temperature: 20°.

the peak maxima from the single merged curve was observed, and therefore the equilibrium characteristics of a distribution process were taken as being represented by the data of the retention volumes at peak maxima[11].

This method, which permits one to avoid taking account of the diffusional broadening of asymmetrical peaks, was used successfully in a number of investigations on the determination of distribution isotherms[12,13].

As is evident from Fig. 2, the linear dependence predicted theoretically (eqn. 14) between $K(h)$ and $1/\sqrt{h}$ at sufficiently low concentrations of eluates actually occurs. A deviation from this linear dependence can be observed in the region of very high peaks, this being in agreement with the more generalized eqn. 13. Similar results were obtained for 1,3-butadiene at various initial concentrations of the BC complex in *n*-dodecane (Fig. 3).

According to eqn. 14, all of the linear graphs plotted for various concentrations of the BC complex cut the ordinate at a single point. Indeed, as follows from eqn. 14, the K_0K' intercept on the ordinate (Figs. 2 and 3) is equal to $^1/_2\ K_0K_p$, that is, its length does not depend upon the initial concentration of the complex in solution. The ratios of the slopes of the linear graphs of $K(h)$ *versus* $1/\sqrt{h}$ plotted for various concentrations of substance BC in solution are mainly proportional to the ratios of corresponding values of $a^{\frac{1}{2}}$ (within 10–15%), this being also in accordance with eqn. 14. When the concentration a increases, the deviation from this proportionality shows little change. Special tests indicated that the dependences remain constant when the carrier gas flow-rate varies from 40 to 100 ml/min, the position of the K' point being unaffected by a two-fold increase in the amount of liquid phase in the column, although the slope of curves becomes somewhat greater (by nearly 7%).

Hence the experimental results confirm that the derived eqns. 13 and 14 are

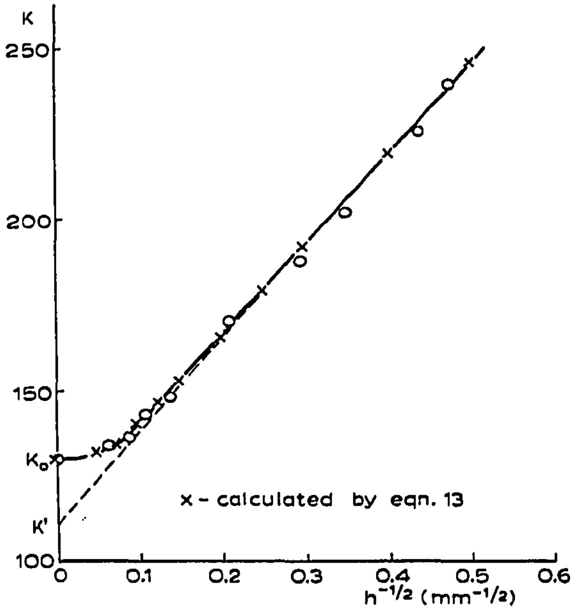


Fig. 2. Dependence of $K(h)$ values corresponding to peak maxima for *cis*-1,3-pentadiene upon the reciprocal of the square roots of their heights ($1/\sqrt{h}$). Stationary phase: solution of (acac)Rh(CO)-(C_8H_{14}) in *n*-pentadecane ($a = 0.02$ M). Temperature: 40°. ○, Experimental points. The curve (×, solid line) is calculated by eqn. 13 at $a = 0.0042$ M and $K_p = 2(K_0 - K')/K_0 = 0.35$; detector constant $\kappa = 0.63 \cdot 10^{-6}$ mole/l·mm.

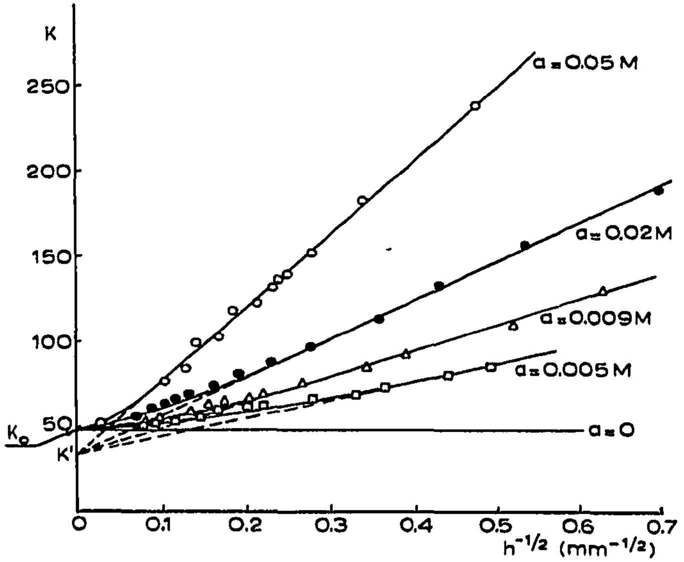


Fig. 3. Dependence of $K(h)$ upon $1/\sqrt{h}$ for 1,3-butadiene samples at various concentrations of (acac)Rh(CO)(C_8H_{14}) in *n*-dodecane. Temperature: 20°.

valid and hence indicate the possibility of easily calculating equilibrium constants of exchange reactions from the K_0K' intercepts on the ordinate in plots of K *versus* $1/\sqrt{h}$.

By using this method, the equilibrium constants of exchange reactions (eqn. 2) of 1,3-butadiene and 1-butene at three temperatures were calculated (Table I).

From the temperature dependence of K_p, the standard enthalpy and entropy changes of these reactions were calculated. The calculated thermodynamic characteristics were found to be close to the corresponding values obtained by a known method by Cramer[14] for the displacement of ethylene by some olefins from acetylacetonatodiethylenerhodium(I). From Cramer's data, $K_p^{25°}$ for 1-butene is 0.09 and ΔH is +1.0 ± 1.4 kcal/mole.

TABLE I

THERMODYNAMIC CHARACTERISTICS OF REACTION 2

Temperature (°C)	*A = 1,3-Butadiene*			*A = 1-Butene*		
	K_p	ΔH^0 *(kcal/mole)*	ΔS^0_{298} *(e.u.)*	K_p	ΔH^0 *(kcal/mole)*	ΔS^0_{298} *(e.u.)*
10	0.5	+1.9 ± 0.5	+5.3	0.18	+4.6 ± 1.0	+13
20	0.57			0.24		
30	0.63			0.31		

It should be noted that this proposed method for investigating the equilibrium of exchange reactions certainly requires further examination. Thus, it remains unclear why the K_p values evaluated from the slopes of $K(h)$ *versus* $1/\sqrt{h}$ graphs (eqn. 14) are sometimes twice or three times smaller than those calculated from the K_0K' intercepts on the ordinate. This is similar to the finding that the concentration of the BC complex in a stationary phase was four to nine times smaller than that in the initial solution before it was added to a solid carrier. Fig. 2 shows the position of points found by eqn. 13 at $a = 0.0042$ M instead of $a = 0.02$ M at $K_p = 0.35$ evaluated from the K_0K' intercept. To judge from the position of these points, eqn. 13 describes reasonably well the character of the experimentally found dependence of $K(h)$ upon $1/\sqrt{h}$ over the whole range of peak heights.

CONCLUSIONS

It has been shown that the equilibrium of exchange reactions can be investigated by the described gas chromatographic method. Using this method, equilibrium constants for the displacement of cyclooctene by 1,3-butadiene and 1-butene from acetylacetonatocarbonylcyclooctenerhodium(I) at 10, 20 and 30° have been calculated.

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