RELATIVE EQUILIBRIUM CONSTANTS FOR IODINE–OLEFIN INTERACTIONS FROM PEAK BROADENING MEASUREMENTS

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Satisfactory gas chromatographic separations usually require the various interactions which determine peak characteristics to occur near equilibrium conditions. As a consequence, techniques for obtaining thermodynamic and related functions have developed exploiting data obtained under good analytical conditions. Thus, retention volumes have been used to obtain thermodynamic quantities for solution processes[1–3] and equilibrium constants for transient complexes[4–8].

Abnormally large height equivalent to a theoretical plate values have been observed in some chromatographic systems where complexes are believed to form between the eluents and the active agent of the column[6,9,10]. Variations in peak width with molecular structure were particularly evident in our recent study of electron-donor–acceptor interactions of molecular iodine with olefins[8]. When the theoretical plate concept is applied to a hypothetical column, it is readily shown that peak broadening results when the rates of interphase transfer of the sample are slow relative to the residence time, so that rapid equilibration can no longer be assumed. Nonequilibrium chromatographic processes have been considered quantitatively by a variety of mathematical techniques[11]. The treatment of YAMAZAKI[12] which uses the Mellin transform to obtain successive moments of the distribution function provides mathematical descriptions of peak characteristics readily comparable with experiment.

Either lack of rapid equilibration of the adsorption and desorption processes relative to the carrier gas flow or the formation of iodine–olefin compounds which form and decompose relatively slowly may cause the abnormally large height equivalent to a theoretical plate values observed for some olefins, especially terminal *n*-olefins, on iodine columns. The experimental data for peak broadening are unfortunately cruder than retention volume data, but nevertheless, it is instructive to analyze the peak broadening phenomena and to calculate relative equilibrium constants from these data for comparison with similar constants previously obtained from retention times alone[8].

EXPERIMENTAL

Retention times and peak widths for a variety of paraffins and unsaturated hydrocarbons have been determined on the columns described in Table I. Details of

TABLE I

DESCRIPTION OF SOLID IODINE COLUMNS

Column	Solid support	Weight % iodine	Physical description
I	Silanized firebrick, 60–80 mesh Chromosorb P AW, DMCS	19.8	20 ft. stainless steel 0.125 in. O.D.
II	Silanized Celite, 60–80 mesh Diatoport S	19.7	20 ft. stainless steel 0.125 in. O.D.
III	Firebrick, 42–60 mesh Chromosorb P	19.2	20 ft. stainless steel 0.125 in. O.D.
IV	Firebrick, 30–60 mesh Chromosorb P	19.9	16 ft. Pyrex 4 mm I.D.

column preparation and of experimental technique have been reported previously[8], and only salient features are given here. All measurements were at $0°$. Most materials were Phillips Petroleum Company pure or research grade hydrocarbons, and 10^{-3} to 10^{-1} μmole samples gave an adequate signal with flame ionization detection and 1 mV recorder display. Injection was rapid ($<$ 1 sec) compared with peak widths.

Flow rates were calculated from methane retention times, and are averages over the entire column length. Because retention times of methane, ethane, and ethylene are almost indistinguishable, it seems justifiable to assume that methane does not interact with the column packings under the conditions used. Frequent injections of methane and 2,3-dimethylbutane provided controls of flow rate and column operating conditions. Minor adjustments for slight deviations from standard conditions have been made to the tabulated data (Tables II and III) where appropriate.

Peak widths were measured along the base line between the extrapolated tangents to the points of inflection on either side of the peaks. Retention times were taken at the points of intersection of these tangents, which agreed closely with the peak height maxima. Despite the skewness of some of the peaks, retention times and peak widths were generally well defined and varied little with sample size for the small samples used to obtain the data. However, for very broad peaks (e.g., those for the terminal olefins), larger samples, sometimes approaching 10^{-1} μmole, were needed to obtain a useable detector response, and the estimation of retention parameters became more subjective. All measurements were made at least on duplicate experiments, and four to eight or more repeat runs of those peaks most prone to error were examined.

RESULTS

Because the same columns have been used to obtain the data needed to calculate equilibrium constants from peak width measurements as were used in deriving these constants from retention times alone, the arguments that were previously advanced[8] concerning the relative reliability of the data from the various columns also apply in this study. The most reliable data are for Columns I and II, especially when adjusted retention times ($t'_r = t_r - t_0$ where $t_0 = t_r$(methane)) are greater than $\sim$ 0.5 min. However, equilibrium constants derived from retention data on the untreated firebrick–iodine Columns III and IV are valuable in illustrating the selfconsistency of the data despite the experimental uncertainties and are therefore included.

TABLE II

RETENTION TIMES (t_r) AND HEIGHT EQUIVALENT TO A THEORETICAL PLATE VALUES (H) FOR PARAFFINS AND CYCLOPARAFFINS ON SOLID IODINE AT 0°

Hydrocarbon	t_r (min)						H (cm)					
Column[a]	I			II	III	IV	I			II	III	IV
Flow rate (cm sec⁻¹)	0.92	1.93	4.43	3.4	5.7	4	0.92	1.93	4.43	3.4	5.7	4
Methane	11.05	5.27	2.30	2.99	1.78	2.03	—	—	—	—	—	—
Propane	11.83	5.59	—	—	2.01	—	1.3	0.78	—	—	0.57	—
Butane	13.49	6.50	2.80	3.11	2.60	2.93	1.2	0.66	0.38	0.47	0.66	0.49
2-Methylpropane	12.78	6.13	2.67	3.08	2.45	—	1.0	0.68	0.39	0.45	0.68	—
Pentane	18.12	8.82	3.80	3.35	4.98	5.54	1.4	0.78	0.57	0.61	—	0.51
2-Methylbutane	16.56	7.97	3.49	3.31	4.39	4.83	1.0	0.56	0.40	0.48	0.43	0.63
Hexane	34.2	16.1	6.90	4.29	—	—	2.5	1.8	1.3	1.9	—	—
2-Methylpentane	16.6	13.3	5.64	3.91	—	—	1.1	0.65	0.63	0.62	—	—
2,3-Dimethylbutane	26.0	12.32	5.37	3.79	10.7	11.0	1.0	0.55	0.54	0.54	0.47	0.61
Cyclopropane	—	5.88	—	3.06	2.11	—	—	1.0	—	0.58	0.76	—
Cyclopentane	21.8	10.5	4.50	3.61	5.0	5.6	1.8	1.4	0.61	0.84	—	0.61
Cyclohexane	40.9	19.6	8.35	4.49	—	—	1.8	1.3	1.1	1.6	—	—
Cycloheptane	—	59.5	25.7	9.4	—	—	—	4.4	4.4	7.8	—	—

[a] Columns are described in Table I.

The height equivalent to a theoretical plate (H) is calculated from the column length, L, the unadjusted retention time, t_r, and the peak width from the expression

$$H(\text{cm}) = \frac{L(\text{cm})}{16[t_r(\text{min})/\text{peak width (min)}]^2}$$

Retention times and H values for four different solid iodine columns are given in Table II for paraffins and cycloparaffins and in Table III for unsaturated hydrocarbons. Flow rates are also tabulated.

Paraffins and cycloparaffins exhibit normal chromatographic behavior on iodine columns, but olefins are retained longer and have larger H values than their structurally analogous paraffins. This specific interaction of olefins with the iodine substrate is of special interest, and is ascribed to the formation of a transient olefin–iodine complex. To separate this effect from the superimposed effect of the size of the molecule (which is assumed to be equal for structurally analogous paraffins and olefins) the overall adsorption process is described by the following equilibria,

$$
A'_c \underset{k'_{-c}}{\overset{k'_c}{\rightleftarrows}} A'_s \underset{k'_{-s}}{\overset{k'_s}{\rightleftarrows}} A \underset{k_{-s}}{\overset{k_s}{\rightleftarrows}} A_s \underset{k_{-c}}{\overset{k_c}{\rightleftarrows}} A_c
$$

$$\underbrace{}_{\substack{V'_s \text{ (exposed} \\ \text{support)}}} \quad \underbrace{}_{V_g \text{ (gas phase)}} \quad \underbrace{}_{\substack{V_s \text{ (solid} \\ \text{iodine)}}}$$

where A stands for a hydrocarbon molecule (olefin or paraffin), A_s is a molecule adsorbed on iodine (without being complexed), A_c is a molecule complexed with iodine, A'_s and A'_c are, respectively, the molecules adsorbed and complexed on the exposed "support"; V_g, V_s, and V'_s are the volume elements corresponding to the gas, iodine, and the exposed "support" phases, respectively. The following equilibrium constants are defined:

$$K_s = [A_s]/[A], \quad K_c = [A_c]/[A_s], \quad K_a = K_s K_c = [A_c]/[A],$$

and

$$K'_s = [A'_s]/[A], \quad K'_c = [A'_c]/[A'_s], \quad K'_a = K'_s K'_c = [A'_c]/[A].$$

For this system, assuming continual equilibration and a plane source, it has been shown[8] that

$$\frac{t_r}{t_0} = 1 + \alpha K_s(1 + K_c) + \alpha' K'_s(1 + K'_c) \tag{1}$$

where α (and α') is the volume ratio V_s/V_g (and V'_s/V_g), and $t_0 = L/U$ (with $U =$ linear flow rate of carrier gas). To calculate equilibrium constants, the following assumptions were made: (1) for an olefin and its structurally analogous paraffin $K_s(\text{ol}) = K_s(\text{par})$ and $K'_s(\text{ol}) = K'_s(\text{par})$, (2) $K_c(\text{par}) = K'_c(\text{par}) = 0$, and (3) $K'_c(\text{ol}) = 0$. With one olefin chosen as standard (*cis*-butene-2 was chosen in ref. 8, and is also taken as reference material in this discussion. Values for the standard are indicated by asterisks), the relative values for the equilibrium constants are

$$K_a/K^*_a = [t_r(\text{ol}) - t_r(\text{par})] / [t_r(\text{ol}) - t_r(\text{par})]^* \tag{2}$$

TABLE III

RETENTION TIMES (t_r) AND HEIGHT EQUIVALENT TO A THEORETICAL PLATE VALUES (H) FOR UNSATURATED HYDROCARBONS ON SOLID IODINE AT 0°

Hydrocarbon	t_r (min)						H (cm)					
Column[a]	I	I	I	II	III	IV	I	I	I	II	III	IV
Flow rate (cm sec^{-1})	0.92	1.93	4.43	3.4	5.7	4	0.92	1.93	4.43	3.4	5.7	4
RCH=CH₂												
Ethylene	11.05	5.27	—	2.99	1.80	2.07	—	—	—	—	—	—
Propylene	15.98	8.49	2.48	3.05	10.7	8.8	27.6	27.6	0.58	1.8	234	507
Propylene-d_6	19.10	10.34	2.48	3.15	21.4	—	41.1	50.7	0.63	1.9	203	—
Butene-1	37.2	21.9	5.08	4.62	93	35.3	30.4	21.7	152	27.6	19	76
Pentene-1	93.6	37.5	12.7	5.73	—	92	10.1	16.0	69.2	30.4	—	—
3-Methylbutene-1	35.7	20.6	5.9	4.68	—	50.7	19	14.5	117	13.2	—	60.8
R₂C=CH₂												
2-Methylpropene	14.46	6.95	2.98	3.13	5.76	4.03	1.32	0.76	0.63	0.52	1.4	1.7
2-Methylbutene-1	22.8	10.87	4.59	3.63	—	11.1	1.60	1.08	1.12	0.82	—	1.52
2-Methylpentene-1	39.3	19.0	8.18	4.53	—	—	1.90	1.27	2.76	1.32	—	—
cis-RCH=CHR												
cis-Butene-2	19.70	9.82	4.01	3.51	22.5	8.8	2.76	2.45	3.8	1.08	3.5	11.7
cis-Butene-2-d_8	21.7	10.99	4.38	3.85	33.6	12.8	3.38	2.76	11.2	1.52	3.5	—
cis-Pentene-2	42.7	20.27	8.04	4.77	92	30	3.04	3.80	5.74	5.97	—	2.53

trans-RCH=CHR												
trans-Butene-2	15.10	7.26	3.15	3.23	5.66	4.03	1.69	1.08	1.01	0.66	3.9	—
trans-Butene-2-d_8	15.35	7.31	3.17	3.27	7.08	4.37	1.79	1.13	1.13	0.63	5.43	—
trans-Pentene-2	23.0	10.87	4.60	3.64	16.3	9.7	2.17	1.32	1.52	0.92	—	3.38
R_2C=CHR												
2-Methylbutene-2	23.2	10.97	4.70	3.58	12.8	8.5	1.60	0.98	0.89	0.82	0.60	1.01
2-Methylpentene-2	41.6	20.0	8.72	4.57	—	—	1.52	1.05	2.34	1.38	—	—
R_2C=CR_2												
2,3-Dimethylbutene-2	47.3	23.1	10.22	4.97	—	24.3	2.03	1.60	2.17	1.90	—	—
Cycloolefins												
Cyclopentene	35.5	17.1	6.85	4.41	—	15	5.63	5.63	3.8	3.54	—	6.08
Cyclohexene	—	140	64.6	35	—	218	—	9.21	16	67.5	—	—
Cycloheptene	—	80	34.9	13.5	—	86	—	7.24	6.08	12.7	—	—
Diolefins												
Butadiene-1,3	20.71	11.27	3.78	3.64	19.6	8.3	8.0	12.2	28.7	5.43	43.4	33.8
Butadiene-1,3-d_6	24.3	14.22	4.53	3.97	—	11.2	14.5	19.0	50.7	1.08	—	61
Acetylene derivatives												
Acetylene	—	—	2.45	3.02	1.88	—	—	—	—	—	—	—
Methylacetylene	14.70	7.12	3.11	3.11	3.78	—	1.9	1.4	1.01	0.69	0.43	—
Methylacetylene-1-d_1	14.70	7.12	3.11	—	—	—	1.9	1.4	1.01	—	—	—
Aromatic hydrocarbons												
Benzene	81.3	37.0	16.4	6.7	—	—	7.42	7.60	9.50	6.47	—	—
Toluene	—	—	13.1	—	—	—	—	—	30.4	—	—	—

a Columns are described in Table I.

If assumption (3) that olefins do not complex with the support is not valid, *i.e.*, $K'_c \neq 0$, but if olefins interact with the exposed support in the iodine coated columns exactly as they do with uncoated support, then

$$K_a/K^*_a = [t_r(\text{ol}) - \rho t_r(\text{par})]/[t_r(\text{ol}) - \rho t_r(\text{par})]^* \tag{3}$$

where $\rho = t'_n = (t_r - t_0)_{\text{ol}}/(t_r - t_0)_{\text{par}}$ for the uncoated support material. The normalized retention time, t'_n, is a measure of the interaction of olefins relative to their structurally analogous paraffins[6].

YAMAZAKI[12], in general agreement with other workers[11], obtains the following expression for the excess, h, in the height equivalent to a theoretical plate (H) due to nonequilibration of the adsorption and desorption processes on several adsorption sites, i,

$$h = H - \frac{2D}{U} = \frac{2U \sum \alpha_i k_i/(k_{d_i})^2}{(1 + \sum \alpha_i k_i/k_{d_i})^2} \tag{4}$$

where D is the diffusion constant and k and k_d are respectively the rate constants of adsorption and desorption. Also, he obtains

$$t_r/t_0 = 1 + \sum \alpha_i k_i/k_{d_i} \tag{5}$$

which is equivalent to eqn. (1) for two sites.

In the present case two adsorption sites are considered: iodine (with rate constants for overall adsorption and desorption k and k_d), and the exposed support (with corresponding rate constants k' and k'_d), so that

$$h t_r^2/t_0^2 = 2U[\alpha k/(k_d)^2 + \alpha' k'/(k'_d)^2] \tag{6}$$

The values of $\alpha(\alpha = V_s/V_g)$ and $\alpha'(\alpha' = V'_s/V_g)$ cannot be known and in order to make use of eqn. (6) it is necessary to introduce some simplifying assumptions. In the following it is assumed that for an olefin and its structurally analogous paraffin

$$(k')_{\text{ol}} = (k')_{\text{par}} \text{ and } (k'_d)_{\text{ol}} = (k'_d)_{\text{par}}$$

Under such conditions and for a given column, *i.e.*, assuming α and α' to remain invariant, eqns. (5) and (6) become

$$\left(\frac{t_r}{t_0}\right)_{\text{ol}} - \left(\frac{t_r}{t_0}\right)_{\text{par}} = \alpha \left\{ \left(\frac{k}{k_d}\right)_{\text{ol}} - \left(\frac{k}{k_d}\right)_{\text{par}} \right\} \tag{7}$$

and

$$\left(\frac{h t_r^2}{t_0^2}\right)_{\text{ol}} - \left(\frac{h t_r^2}{t_0^2}\right)_{\text{par}} = 2U\alpha \left\{ \left(\frac{k}{k_d^2}\right)_{\text{ol}} - \left(\frac{k}{k_d^2}\right)_{\text{par}} \right\} \tag{8}$$

From (8) and (7) it follows that

$$\eta = \frac{(h t_r^2)_{\text{ol}} - (h t_r^2)_{\text{par}}}{[(t_r)_{\text{ol}} - (t_r)_{\text{par}}]^2} = \frac{2\left[\left(\frac{k}{k_d^2}\right)_{\text{ol}} - \left(\frac{k}{k_d^2}\right)_{\text{par}} \right]}{\left[\left(\frac{k}{k_d}\right)_{\text{ol}} - \left(\frac{k}{k_d}\right)_{\text{par}} \right]^2} \times U = \text{const} \times U \tag{9}$$

To evaluate approximately η it is further assumed that $H \gg 2D/U$. Then eqn. (9) requires that η should be a linear function of U. The data obtained with Column I at three different values of U can be used in principle to test this prediction; however, although in many cases a qualitative agreement is found, the experimental scatter turns out to be much too large for a stringent test of eqn. (9). Perhaps with the columns used in this work the values of α and α' may vary over a period of time for wide variations of working conditions as a result of the relatively high volatility of solid iodine. A better consistency may be expected for data such as those in Tables II and III which are obtained simultaneously or in close succession on the same column and at a single flow rate.

Relative to a structurally analogous standard olefin–paraffin pair (*cis*-2-butene and *n*-butane in the present case), eqn. (7) reduces to

$$\frac{(t_r)_{ol} - (t_r)_{par}}{[(t_r)_{ol} - (t_r)_{par}]^*} = \frac{(k/k_d)_{ol} - (k/k_d)_{par}}{[(k/k_d)_{ol} - (k/k_d)_{par}]^*} = \frac{K_a}{K^*_a} \tag{10}$$

Since $(k/k_d)_{ol} = (K_s)_{ol} + K_a$, $(k/k_d)_{par} = (K_s)_{par}$ and it is assumed that $(K_s)_{ol} \approx (K_s)_{par}$, eqn. (10) is identical with eqn. (2).

To make use of eqn. (8) it is necessary to make some assumptions regarding the individual relation between k and k_d and the rate constants k_s, k_{-s}, k_c, k_{-c} entering into the postulated equilibria. For the paraffins, $k/k_d = K_s$, since $K_c = 0$, and therefore, $k = k_s$, $k_d = k_{-s}$. For the olefins, $k/k_d = K_s(1 + K_c)$ and the simplest assumption is that $k = k_s$, $k_d = k_{-s}/(1 + K_c)$, *i.e.*, complexing with iodine does not affect the *rate of adsorption* of olefins but it does decrease their *rate of desorption*. If $K_c \gg 1$ and assuming as before, that $K_s(ol) = K_s(par)$, then eqn. (8) reduces to

$$F = \frac{(ht_r^2)_{ol} - (ht_r^2)_{par}}{[(ht_r^2)_{ol} - (ht_r^2)_{par}]^*} = \frac{(k/k_d^2)_{ol} - (k/k_d^2)_{par}}{[(k/k_d^2)_{ol} - (k/k_d^2)_{par}]^*} \approx \frac{(k^*_d)_{ol}}{(k_d)_{ol}} \frac{K_a}{K^*_a}. \tag{11}$$

Then for olefins, it follows that

$$k_d/k^*_d = (K_a/K^*_a)/F \tag{12}$$

and since $k/k_d = K_a$,

$$k/k^* = (K_a/K^*_a)^2/F \tag{13}$$

If $k_s(= k) = k^*_s(= k^*_s)$, as would be the case if adsorption were very efficient, then eqn. (13) reduces to

$$K_a/K^*_a = F^{1/2} \tag{14}$$

Table IV lists K_a/K^*_a values calculated from eqn. (14) for three flow rates on Column I and at single flow rates on each of Columns II, III and IV and compares these values with K_a/K^*_a previously calculated from eqns. (2) (or (10)) and (3), assuming again that $h \approx H$. Relative equilibrium constants for complexing of adsorbed olefins with iodine can be calculated from the data tabulated in Table IV, since

$$K_c/K^*_c = (t'^*_r/t'_r)_{par}(K_a/K^*_a) \tag{15}$$

TABLE IV

RELATIVE OVERALL EQUILIBRIUM CONSTANTS (K_a) FOR GASEOUS OLEFINS WITH SOLID IODINE AND RELATIVE RATE COMPLEXES AT $0°$[a]

Hydrocarbon	K_a/K^*_a (Equation 14)						K_a/K^*_a	
Column[b]	I			II	III	IV	Eqn.	Eqn.
Flow rates (cm sec^{-1})	0.92	1.93	4.43	3.4	5.7	4	(2)[c]	(3)[c]
RCH=CH$_2$								
Propylene	2.6	3.1	—	—	3.9	—	0.8	0.9
Propylene-d_6	4.1	5.1	—	—	7.3	—	1.3	1.5
Butene-1	7.7	7.1	8.2	8.2	9.6	10.2	4.2	5.2
Pentene-1	12.1	10.4	13.9	12.6	—	—	10.4	12.7
3-Methylbutene-1	5.8	5.4	8.4	5.7	—	13.1	3.5	4.3
R$_2$C=CH$_2$								
2-Methylpropene	0.34	0.23	0.22	0.31	0.15	—	0.26	0.16
2-Methylbutene-1	0.84	0.67	0.57	0.80	—	0.44	0.92	0.80
2-Methylpentene-1	1.0	1.3	1.7	1.4	—	—	1.9	1.4
cis-RCH=CHR								
cis-Butene-2	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
cis-Butene-2-d_8	1.3	1.2	1.9	1.4	1.5	—	1.3	1.5
cis-Pentene-2	2.8	2.7	2.5	2.9	—	1.6	3.6	4.0
trans-RCH=CHR								
trans-Butene-2	0.41	0.37	0.35	0.51	0.26	—	0.26	0.22
trans-Butene-2-d_8	0.46	0.39	0.38	0.49	0.39	—	0.28	0.25
trans-Pentene-2	0.94	0.68	0.64	0.78	—	0.58	0.69	0.56
R$_2$C=CHR								
2-Methylbutene-2	0.87	0.63	0.50	0.78	0.23	0.26	1.0	0.45
2-Methylpentene-2	1.7	1.2	1.7	1.5	—	—	2.3	0.58
R$_2$C=CR$_2$								
2,3-Dimethylbutene-2	2.4	1.9	1.9	2.1	—	—	3.5	0.93
Cycloolefins								
Cyclopentene	3.0	2.7	1.7	2.6	—	1.2	2.1	2.3
Cyclohexene	—	30	34	(98)[d]	—	—	41	48
Cycloheptene	—	12	9	(14)[d]	—	—	7.0	7.7
Diolefins								
Butadiene-1,3	1.9	2.7	2.6	2.8	3.1	1.6	1.1	1.3
Butadiene-1,3-d_6	3.2	4.3	4.2	(1.2)[d]	—	2.9	1.8	2.1
Acetylene derivatives								
Methylacetylene	0.48	0.47	—	—	(0.05)[d]	—	0.46	0.56
Methylacetylene-d_1	0.48	0.47	—	—	—	—	0.46	0.56
Aromatic hydrocarbons								
Benzene	8.7	6.9	6.5	5.5	—	—	6.1	2.5
Toluene	—	—	—	19.8	—	—	—	—

[a] cis-Butene-2 is taken as standard, equal to 1.000.
[b] Columns are described in Table I.
[c] Average values taken from ref. 8.
[d] Broad peaks and/or small t_r values make the data in parentheses less quantitative than the other tabulated values.

CONSTANTS FOR COMPLEX FORMATION (k_c) AND DECOMPOSITION (k_{-c}) FOR ADSORBED OLEFIN–SOLID IODINE

| k_c/k^*_c | | | | | | k_{-c}/k^*_{-c} | | | | | |
| I | | | II | III | IV | I | | | II | III | IV |
0.92	1.93	4.43	3.4	5.7	4	0.92	1.93	4.43	3.4	5.7	4
0.22	0.30	—	—	0.05	—	0.10	0.09	—	—	0.03	—
0.26	0.27	—	—	0.07	—	0.07	0.05	—	—	0.02	—
0.24	0.42	(0.05)[d]	0.21	0.22	0.29	0.06	0.09	(0.03)[d]	0.06	0.05	0.05
0.34	0.24	(0.10)[d]	0.14	—	—	0.08	0.08	(0.04)[d]	0.05	—	—
0.13	0.22	(0.02)[d]	0.13	—	0.13	0.09	0.13	(0.03)[d]	0.10	—	0.05
0.87	1.6	1.8	(0.24)[d]	1.4	—	2.3	4.6	5.4	(1.4)[d]	7.1	—
0.62	0.80	1.1	0.39	—	2.0	1.4	2.0	2.8	1.3	—	5.8
0.50	0.26	0.23	0.16	—	—	1.8	1.0	0.74	0.78	—	—
1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
1.0	1.3	0.5	1.7	1.1	—	0.78	0.95	0.36	0.42	0.71	—
0.73	0.56	0.62	0.34	—	1.8	0.52	0.47	0.56	0.24	—	1.7
0.39	0.38	0.69	0.34	0.33	—	1.5	1.7	2.4	1.1	2.2	—
0.43	0.37	0.67	0.66	0.35	—	1.4	1.5	2.2	1.6	1.5	—
0.24	0.27	0.35	0.29	—	0.38	0.87	1.3	1.6	1.2	—	2.1
0.70	0.94	1.6	0.28	1.1	1.9	1.5	2.3	3.9	1.1	8.2	9.7
0.28	0.42	0.35	0.16	—	—	0.83	1.4	0.92	0.76	—	—
0.32	0.49	0.71	0.29	—	—	0.57	0.87	1.1	0.66	—	—
0.12	0.13	0.31	0.12	—	0.43	0.25	0.28	0.70	0.30	—	1.1
—	0.13	0.15	(0.05)[d]	—	—	—	0.04	0.04	(0.01)[d]	—	—
—	0.01	0.02	(0.01)[d]	—	—	—	0.04	0.10	(0.05)[d]	—	—
0.39	0.27	0.10	0.22	0.08	0.33	0.32	0.19	0.12	0.17	0.09	0.36
0.30	0.29	0.11	—	—	0.23	0.17	0.13	0.08	—	—	0.17
2.8	3.7	—	—	—	—	2.0	2.1	—	—	—	—
2.8	3.7	—	—	—	—	2.0	2.1	—	—	—	—
0.05	0.05	0.08	0.08	—	—	0.09	0.11	0.16	0.18	—	—
—	—	—	—	—	—	—	—	—	—	—	—

Considering the simplifying assumptions which had to be made and the difficulty of determining accurately H and t_r values for the very broad peaks obtained with a number of olefins studied, the K_a/K^*_a values from eqn. (14) (and K_c/K^*_c from eqn. (15)) have adequate correspondence with similar data from ref. 8. It is therefore quite possible that the rates of adsorption do indeed remain approximately constant for various olefins.

However, it is also possible that the difference observed between the equilibrium constants calculated from peak broadening measurements and those from retention data are genuine, *i.e.*, that the rates *of complex formation* may differ appreciably from olefin to olefin. In this case, one refinement of the treatment is to assume that the rate determining steps are the formation (rate constant k_c) and breaking (k_{-c}) of the complex, while physical adsorption (k_s) and desorption (k_{-s}) occur rapidly. With this assumption, the rate of adsorption is $R_a = k_c[A_s] = K_s k_c[A]$. Therefore, $k = K_s k_c$, and eqn. (13) is replaced by

$$k_c/k^*_c = \left(\frac{K_c}{K^*_c} \cdot \frac{K_a}{K^*_a}\right)/F \tag{16}$$

Furthermore, $k/k_d = K_a = (K_s k_c)/k_{-c}$, so that $k_d = k_{-c}$ and eqn. (12) is replaced by

$$k_{-c}/k^*_{-c} = (K_a/K^*_a)/F \tag{17}$$

Equation (17) has been used to calculate k_{-c}/k^*_{-c} values which are also tabulated in Table IV. In principle, the K_c/K^*_c values from eqn. (15) could be used to calculate relative rates of complex formation from eqn. (16), but we believe that the K_c/K^*_c previously reported[8] are more reliable quantitatively, and, therefore, these previous data have been used to obtain the k_c/k^*_c values listed in Table IV ($k_c/k^*_c = (K_c/K^*_c)/(k_{-c}/k^*_{-c})$).

DISCUSSION

YAMAZAKI's equations[12] which relate rates of interphase transfer to excess peak broadening (*i.e.*, the part of the peak width over and above that caused by diffusion broadening alone) enable one to calculate overall equilibrium constants, K_a, and rate constants for adsorption and desorption from chromatographic peak width measurements, and in principle, also from skewness or asymmetry measurements on the peaks. To apply his derivations, near equilibrium conditions must be avoided for the experimental measurements. By making reasonable but fairly extensive assumptions, overall equilibrium constants for complexing of a number of structurally different olefins with solid iodine have been estimated relative to *cis*-butene-2 using height equivalent to a theoretical plate measurements. From the same experimental data, relative rate constants for the forward and reverse interactions have also been calculated. Constants thus calculated from peak width measurements provide an independent set of values to compare with those calculated from retention measurements. To date, it has not been feasible to extract from peak asymmetry characteristics a third set of constants for intercomparison.

The self-consistency of the relative overall equilibrium constants K_a/K^*_a in

Table IV suggests that the approximations required to calculate these data using YAMAZAKI's equations are indeed reasonable and not too drastic. This belief is strengthened by the correspondence between the constants thus calculated and those obtained in ref. 8 directly from retention times. The trends exhibited by the two sets of equilibrium constants are very similar, and except for propylene, the K_a/K^*_a constants agree at least within a factor of two, and generally are much closer. The previously observed[8] secondary deuterium isotope effects are also reproduced.

The correlation between the two sets of K_a/K^*_a values indicates that those factors which determine the retention times of an olefin on a solid iodine column also dictate the extent of excess peak broadening in the column. It will be interesting if this observation can be extended to include peak shapes, i.e., skewness and kurtosis, as is suggested by YAMAZAKI's treatment[12].

The chemical significance of the trends in complex stability has already been discussed[8], and therefore is not considered here.

The quantitative significance of the rate constants for complex formation (k_c) and complex decomposition (k_{-c}) is somewhat questionable. As expected, the terminal olefins exhibit slow complexing and especially slow complex decomposition. Cyclo-olefins and aromatics are likewise slow in making and breaking complexes, whereas those olefins branched at the double bond tend to be relatively faster. Increasing molecular size also appears to reduce the relative rates. However, the scatter is considerable and these values must be evaluated with this scatter in mind.

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SUMMARY

The equations obtained by YAMAZAKI to describe retention characteristics under nonequilibrium chromatographic conditions have been applied to the iodine–olefin system. Starting from these equations, relative overall equilibrium constants for the interactions of gas phase olefins with solid iodine at 0° have been estimated from measurements of excess peak broadening. These data closely resemble similar constants obtained from retention time measurements alone. Relative rates for complex formation and complex decompostion have also been derived from height equivalent to a theoretical plate data. The same factors are believed to determine both retention time and excess peak width under nonequilibrium conditions.

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