GAS–SOLID ADSORPTION CHROMATOGRAPHY OF SOME AROMATIC HYDROCARBONS AND NITROGEN HETEROCYCLES ON ALUMINA

L. H. KLEMM AND S. K. AIREE

Department of Chemistry, University of Oregon,
Eugene, Oreg. (U.S.A.)

In previous papers[1,2] we proposed that aromatic hydrocarbons are adsorbed preferentially flatwise, by means of the π-electron system, on to an alumina surface while aromatic nitrogen heterocycles are adsorbed preferentially edgewise or tilted, by means of the non-bonding (n-)electrons of the nitrogen atom, on to such surface. If substituents on the aromatic ring(s) or the general geometry of the ring system were to cause sufficient steric hindrance to such manners of adsorption adsorbability would be decreased. In the case of a parent aromatic nitrogen heterocycle, in particular, insertion of appropriately located substituents might cause a change from n-type adsorption to π-type or to πn-hybrid type adsorption. From studies on linear elution adsorption chromatography SNYDER[3] has reached similar conclusions on the geometry of adsorption of arenes though he does not, in general, believe that *bona fide* π-complexation is involved. In addition, he has proposed that localization of the anchoring site on the molecule occurs in aromatic nitrogen heterocycles which are, nonetheless, also held flatwise. GILES AND McKAY[4], on the other hand, proposed that arenes are adsorbed in small clusters, stacked face-to-face and edge-on to the surface, for the alumina which they used. The present research was conducted in an effort to gain further insight into these questions of geometry of adsorption, but using gas–solid adsorption elution chromatography instead of liquid–solid adsorption chromatography as used in the previous studies. Compounds investigated were largely confined to the benzene, naphthalene, pyridine, and quinoline systems.

EXPERIMENTAL

Naphthalene, acenaphthene, and the isomeric dimethylnaphthalenes were available in analytically pure form from other studies[5]. Quinuclidine was synthesized by a five-step procedure. Thus, isonicotinic acid (Distillation Products Industries) was converted to ethyl isonicotinate by refluxing with absolute ethanol into which anhydrous hydrogen chloride was passed. Following the procedure of STERNBACH AND KAISER[6], except that catalytic hydrogenation of the intermediate 1-carboethoxy-methyl-4-carboethoxypyridinium bromide was conducted at 2–5 atm pressure instead of at 70 atm as reported, this ester was transformed into 3-quinuclidone. 3-Quinuclidone was reduced to quinuclidine (isolated as the hydrochloride and purified

via the picrate) by the HUANG-MINLON reaction[7]. Other compounds used were available from commercial sources and were fractionally distilled before use.

Chromatography was conducted by means of an F and M model 202 programmed gas chromatograph using copper spiral columns (64 mm internal diameter) packed with F and M 30–60 mesh alumina as adsorbent and helium (passing at the rate of 40 ml/min, as measured at 25° and an inlet pressure of 3.0 ± 0.2 atm absolute) as eluting carrier gas. A thermal conductivity cell was employed as the detector. During each run the column was maintained at a constant temperature (between 173° and 367°) by means of a cylindrical oven surrounding the column. Prior to starting a series of runs at some particular temperature the column was maintained at a temperature at least 25° higher than that of the runs for 3 h or longer. The column temperature as read from the instrument panel was corrected by use of a calibration chart, wherein the true temperature was taken as that determined potentiometrically under steady-state operating conditions and sensed by means of a thermocouple placed at the geometric center of the column spiral. In general, liquid samples were introduced neat by means of a calibrated syringe. Solid samples and some of the less volatile liquids were introduced as solutions in benzene or cyclohexane.

Chromatograms exhibited sharp leading and broad trailing boundaries as are characteristic of gas–solid adsorption chromatography[8]. Since in certain cases maxima were ill-defined, the measured retention time (uncorrected), t_R, was taken as the time elapsed between the initial rise of the air peak and the initial rise of the chromatogram proper. Values of t_R for a variety of cyclic compounds investigated in an exploratory manner are given in Table I. In cases studied more extensively t_R was determined as a function of sample size (0–9 μl for neat liquids, 0–80 μl for solutions) for each compound at each temperature. Except for smaller samples (0–2 μl and 0–20 μl, respectively), which showed positive deviations in t_R, t_R increased linearly with decreasing sample size[9]. The linear portion of the curve was extrapolated to zero sample-size to yield the intercept, $t_R'^{\circ}$. The slope of this linear portion was found to vary with the compound used and to increase algebraically with increasing temperature of the column. Compared to curves for hydrocarbons, 2,6-lutidine (the only nitrogen heterocycle so studied) showed exceptionally large negative slopes at all temperatures. Although t_R was easily measured to an accuracy of ± 0.05 min, the long extrapolation to zero sample-size decreased the estimated accuracy in $t_R'^{\circ}$ to ± 0.2 min for neat liquid hydrocarbons, ± 0.4 min for 2,6-lutidine, and ± 0.8 min for solutions. Using 5 % (w/v) solutions in cyclohexane, a column length of 61 cm, and a temperature of 362° acenaphthene and all of the ten possible dimethylnaphthalenes gave experimentally indistinguishable values of 8.0 ± 1.0 min for $t_R'^{\circ}$, as compared to a value of 3.0 min for naphthalene itself.

Where extrapolated retention times were to be compared at different column temperatures correction was made for the change in rate of flow of the carrier gas due to thermal expansion upon its entering the column. Arbitrarily taking 500° K as a standard of comparison the corrected extrapolated retention time, t_R°, was calculated by means of the relationship

$$t_R^{\circ} = \left[\frac{T}{500}\right] t_R'^{\circ},$$

where T is the column temperature in °K. No correction to t_R° was made for pressure

drop in the column. In Tables II and III are presented data on $t_R°$ for benzene, substituted benzenes, naphthalene, and 2,6-lutidine at various column temperatures and using the regular F and M alumina as well as this alumina pre-treated with quinuclidine. Figs. 1 and 2 show plots of log $t_R°$ *versus* 1000/T, made partially from data given in Tables II and III.

<div align="center">DISCUSSION</div>

It was originally noted by JAMES AND MARTIN[10] that the retention time for a substrate in gas–liquid partition chromatography should increase with increasing molecular weight (*i.e.* with decreasing volatility or increasing boiling point) of the substrate and with increasing interaction (attraction) between the substrate and the stationary phase. For gas–solid adsorption chromatography a similar relationship should hold.

<div align="center">TABLE I</div>

<div align="center">MISCELLANEOUS EXPLORATORY CHROMATOGRAPHIC RUNS</div>

Compounds listed together in one group were all run on the same column in close succession, although not necessarily in the order given. Strongly retained compounds were removed by temperature programming before subsequent compounds in the group were investigated. All columns were 122 cm long. Boiling points are taken from standard references.

Compound	B.p. (°C)	Column temperature (°C)	Sample size (μl)	t_R* (min)
p-Xylene	138	227	12.5	5.6
Ethylbenzene	136	227	12.5	5.5
2-Ethylthiophene	134	227	11.5	5.5
2,5-Dimethylthiophene	137	227	11.5	5.6
m-Xylene	139	254	25	5.4
Thiophene	84	254	16	1.5
3-Methylthiophene	115	254	19.2	3.0
2-Ethylthiophene	134	254	22.5	5.1
2,5-Dimethylthiophene	137	254	27.5	4.7
2-Picoline	129	254	19.6	> 90
2,6-Lutidine	143	254	22.8	16.1
Pyridine	116	362	16	> 180
2-Picoline	129	362	19.5	13.9
2-Ethylpyridine	149	362	22	11.5
2,6-Lutidine	143	362	22	1.1
3,5-Lutidine	171	362	22	> 180
Quinoline	238	362	23.5**	> 85
8-Methylquinoline	249	362	27**	7.4
1-Methylisoquinoline	248	362	27**	> 120
2,4-Dimethylquinoline	265	362	29**	36.5
2,6-Dimethylquinoline	267	362	29**	32.0
2,8-Dimethylquinoline	252	362	26**	8.2
2-Methylbenzoxazole	201	362	25.5**	> 48
Quinuclidine***	—	308–394	36	> 180

* For those compounds for which indefinite values are given for t_R, timing was stopped at the t_R shown and the compound was removed from the column by subsequent temperature programming.
** Solution, 25 % (w/v) in benzene.
*** Solution, 10 % (w/v) in benzene. Run with temperature programming. The evolution of quinuclidine started after more than 2 h at 394°.

Observed discrepancies between the order of increasing boiling points and the order of increasing retention time in gas–solid chromatography might then be ascribable to variations in the strengths of adsorption of the substrate molecules on to the solid adsorbent. Examination of Table I shows that several nitrogen heterocycles exhibit unusually large values for t_R. For the series pyridine, 2-picoline, 2,6-lutidine, in particular, the order of increasing t_R is a marked inversion of the order of increasing boiling point.
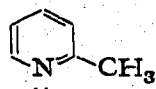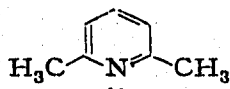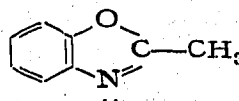
| 2-Picoline | 2,6-Lutidine | 2-Methylbenzoxazole | Quinuclidine |

Also 8-methylquinoline and the three dimethylquinolines studied have t_R less than for quinoline while all of the dimethylnaphthalenes are more strongly retained than is naphthalene. Quinuclidine, moreover, is strongly retained in spite of the facts that its molecular weight approximates that of ethylbenzene and that it sublimes readily on being heated in air. These results are consistent with the group adsorption (geometric) factors noted by SNYDER[3] and with our previous proposal (based on liquid–solid chromatography on alumina) that azacyclic compounds are adsorbed on alumina preferentially by means of the n-electrons on the nitrogen atom. In the pyridine molecule steric hindrance to adsorption is provided by alkyl groups in an α-position but not by ones in a β-position. For quinoline, steric hindrance to adsorption is largest for an alkyl group in the 8-position (where the C_{Ar}–C_{Al} bond is directed parallel to the spatial direction of the n-electrons) and smaller in the 2-position (where corresponding directions make an angle of about 120°). 1-Methylisoquinoline and 2-methylbenzoxazole have even less hindered n-electrons than does 2-methylquinoline. For quinuclidine the alternative possible formation of a π-complex rather than of an n-complex is not present. In contrast to the nitrogen heterocycles the thiophenes studied showed little irregularity (compared to one another or to arenes of similar boiling point) in t_R, consistent with previous observations[2,3,11].

PINES et al.[12] proposed that catalytically active alumina contains two kinds of Lewis acid sites, strong and weak, as determined by the ability or lack of ability, respectively, of the site to effect either skeletal rearrangement of certain alcohols during the process of dehydration or double bond migration in the initially formed alkene. Treatment of the alumina with ammonia or amines served to effect dehydration without skeletal rearrangement, probably because the nitrogen compounds were tenaciously adsorbed to the strong sites, while some weak sites were still available for the dehydration process. In a preliminary effort to investigate the possibility that arenes and azacyclic compounds might be adsorbed on different sites on the alumina surface we have determined values of $t_R°$ at various temperatures for benzene, the alkylbenzenes ØR (where R = Me, Et, Pr, and Bu), m-xylene, naphthalene, and 2,6-lutidine using columns containing, first, plain alumina and then, later, the same alumina after treatment with non-eluting quinuclidine.

Typical data obtained are presented in Tables II and III and plotted in Figs. 1 and 2. Unfortunately, at the upper limit of column temperatures, T, available with our apparatus retention times for all of the aromatic nitrogen heterocycles (other than 2,6-lutidine) of interest were too large to allow suitable determinations of $t_R°$ versus T.

TABLE II

GAS ADSORPTION CHROMATOGRAPHY OF BENZENE AND MONOALKYLBENZENES ON ALUMINA

Compound B.p., °C**	Variables in run	Corrected extrapolated retention time, t_R° (in min)												
	Column* temp °C	243			259			276			292			
		A3 bare	A3 Qt	A4 bare	A3 bare	A3 Qt	A4 bare	A3 bare	A3 Qt	A4 bare	A3 bare	A3 Qt	A4 bare	
Benzene	80.1	1.3	1.2	1.5										
Toluene	110.6	2.9	2.3	3.4	2.0	1.7	2.4		1.3			1.0		
Ethylbenzene	136.2	5.3	5.0	6.2	3.5	3.0	4.6	2.4	2.1	3.2	1.9	1.7	2.4	
Isopropylbenzene	152.4	8.1	6.2		5.0	4.2	6.7	3.7	3.3	4.8	2.6	2.3	3.5	
n-Propylbenzene	159.2	9.4	7.7		5.8	5.4	8.5	4.5	3.8	6.1	3.3	2.9	4.2	
tert.-Butylbenzene	169.1				7.6	6.5		5.3	4.6		3.7	3.1		
sec.-Butylbenzene	173.3				7.9	6.9		5.4	5.2		4.1	3.8		
Isobutylbenzene	172.8	14.2			9.9	8.4		6.4	5.7		4.9	4.1		
n-Butylbenzene	183.3	18.7			11.7	9.8		7.6	6.9	10.2	5.5	4.6	7.3	

* Columns A3 and A4 had the same dimensions (61 cm long) and contained the same weights of alumina (11 g). Column A3 QT resulted from passing 95 μl of a 5% (w/v) solution of quinuclidine in dioxane onto column A3 at 389° and maintaining this temperature for several hours.

** Boiling points were obtained from Selected Values of Properties of Hydrocarbons, Am. Petroleum Inst., Research Project 44.

Examination of Tables II and III shows that for each compound $t_R°$ decreases with increasing T. Also at any particular T, the compound is adsorbed less tenaciously on quinuclidine-treated alumina than on plain (or bare) alumina. Although columns A3 and A4 were prepared in the same manner, $t_R°$ values on them were somewhat different. From Table II one notes that, in general, for a particular column and temperature $t_R°$ increases with increasing boiling point of the alkylbenzene used. The pair isobutylbenzene–sec.-butylbenzene, however, provides an exception to this trend. The inverted order for this pair may be ascribed to a larger steric hindrance by the sec.-butyl group, $–CH(CH_3)C_2H_5$ (as compared to the isobutyl group, $–CH_2CH-(CH_3)_2$), toward flatwise adsorption of the benzene ring. The magnitude of such steric hindrance would be largely dependent upon the relative sizes of the substituents on the carbon atom adjacent to the ring. From Table III one notes that at the common temperature of 292° 2,6-lutidine is retained 2–5 times as long as m-xylene despite the facts that these two substrates have the same symmetry and nearly equal boiling points and molecular shapes.

TABLE III

GAS ADSORPTION CHROMATOGRAPHY OF THREE COMPOUNDS ON ALUMINA

Compound	B.p.* (°C)	Column temp. (°C)	Corrected extrapolated retention time, $t_R°$ (min)			
			Column A3**		Column A4	
			bare	quinuclidine-treated	bare**	quinuclidine-treated***
m-Xylene	139	243	5.6	4.3	6.2	3.6
		259		3.2	4.3	2.5
		276		2.2	3.6	1.8
		292		1.7	2.3	1.5
2,6-Lutidine	143	292	11.9	7.9	9.6	4.0
		308	6.8	4.4	6.0	2.6
		324	5.1	3.1	4.2	1.8
		340	3.6	2.2	3.1	1.4
Naphthalene	218	292				7.5
		308			12.0	5.5
		324			7.7	3.9
		340			6.5	3.1

* Obtained from standard sources.
** See footnote* to Table II.
*** Prepared from column A4 in a manner similar to that used in obtaining column A3 QT.

Following the method of GREENE AND PUST[13] the heats of adsorption, H_{ads}, of the compounds given in Tables II and III were obtained from the slopes of the linear plots in Figs. 1 and 2. It is apparent from a glance at these figures that H_{ads} does not differ greatly from one compound to another. Thus, benzene and the alkylbenzenes give H_{ads}-values of 12.2 ± 2.2 kcal/mole on bare alumina (for both columns used) and of 11.5 ± 2.1 kcal/mole on quinuclidine-treated alumina (for column A3 only). For column A4 the corresponding data are: m-xylene (12.3, 10.8); naphthalene (14.5, 12.7); and 2,6-lutidine (16.0, 13.7)—with an estimated accuracy of ± 0.7 kcal/mole in each value and an average change in H_{ads} on going from bare to quinuclidine-treated alumina of —1.9 kcal/mole. The similarities in the data for 2,6-lutidine and
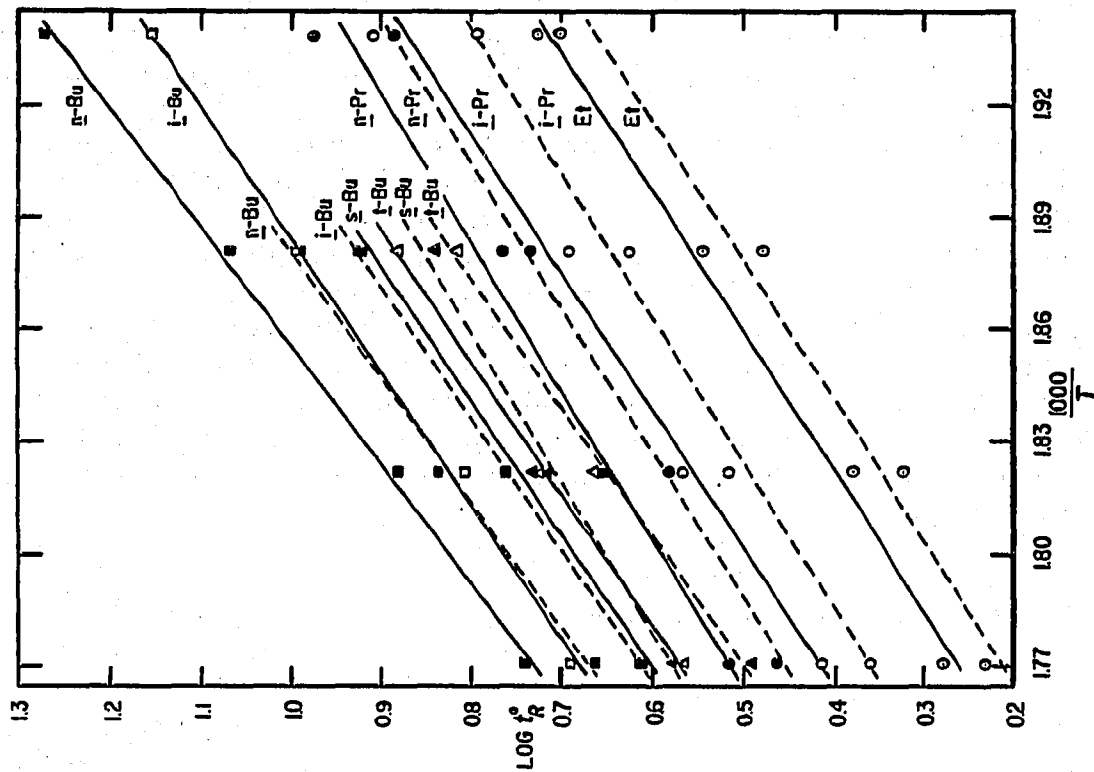
Fig. 2. Plots of log t_R° versus $1000/T$ using column A3. Broken lines refer to quinuclidine-treated column; solid lines, to the bare column for mono-alkylbenzenes.
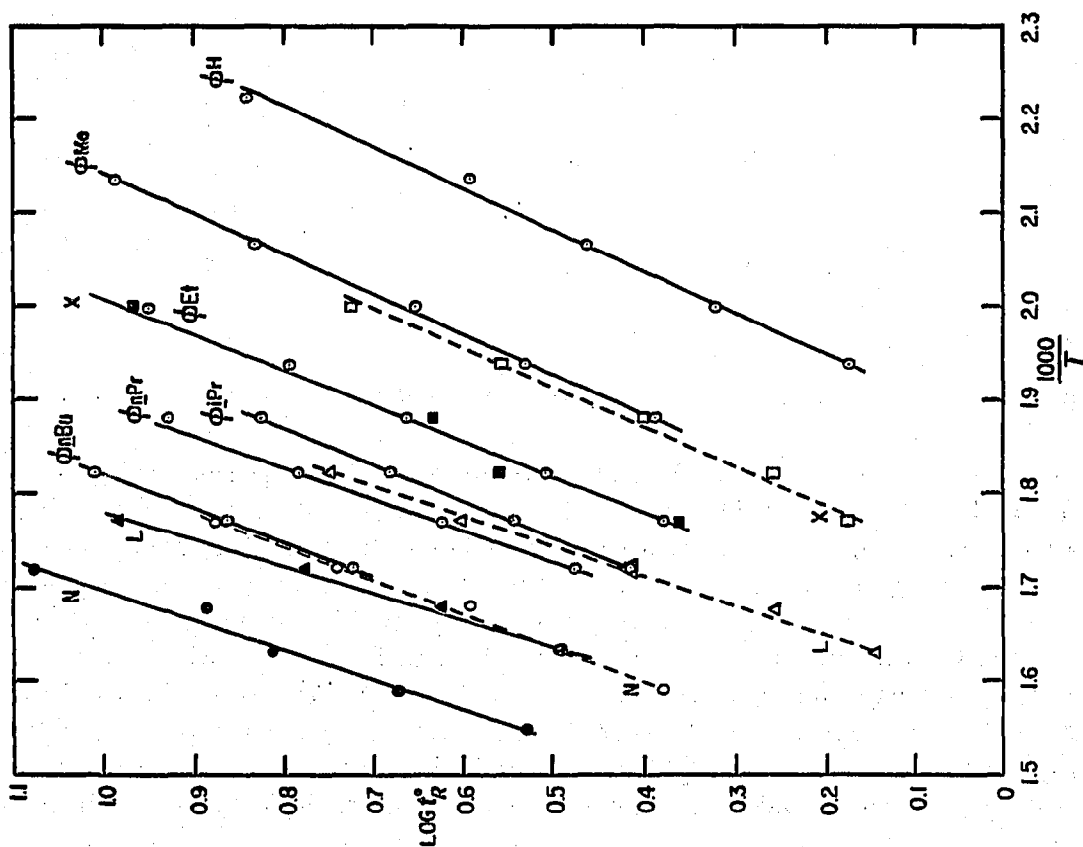
Fig. 1. Plots of log t_R° versus $1000/T$ using column A4. Broken lines refer to quinuclidine-treated column; solid lines, to the bare column. N = naphthalene; L = 2,6-lutidine; X = m-xylene.

m-xylene lead us to believe that both of these compounds are adsorbed preferentially flatwise and that the somewhat larger values in $t_R°$ and H_{ads} for 2,6-lutidine may be ascribed to the greater polarity of the pyridine ring system as compared to the benzene ring system. Further studies with other azacyclic compounds at higher column temperatures will be needed in order to check on this possibility. Meanwhile, however, it should be noted that our measurements are concerned with those molecules of substrate which traverse the column most rapidly and, therefore, probably are adsorbed only the smallest number of times on the energetically weakest adsorption sites. It is conceivable that the geometry of adsorption of an azacyclic compound may vary with the strength (or type) of adsorption site which it occupies on the surface.

SUMMARY

By means of gas-solid adsorption elution chromatography on alumina, either plain or pre-treated with non-eluting quinuclidine, retention times and heats of adsorption were determined for benzene, eight monoalkylbenzenes, m-xylene, naphthalene, and 2,6-lutidine. In general both retention time and heat of adsorption decreased on impregnating the alumina with quinuclidine. For plain alumina various pyridines and quinolines were very strongly retained so long as the non-bonding electrons on the nitrogen atom were not sterically hindered by ring substituents. Results are consistent with data on adsorbabilities obtained earlier from solid–liquid chromatography.

REFERENCES

1 L. H. KLEMM, D. REED, L. A. MILLER AND B. T. HO, J. Org. Chem., 24 (1959) 1468.
2 L. H. KLEMM, E. P. ANTONIADES, G. CAPP, E. CHIANG AND E. Y. K. MAK, J. Chromatog., 6 (1961) 420.
3 L. R. SNYDER, J. Chromatog., 6 (1961) 22; 8 (1962) 319; J. Phys. Chem., 67 (1963) 234, 2344.
4 C. H. GILES AND R. B. McKAY, J. Chem. Soc., (1961) 58.
5 L. H. KLEMM AND A. J. KOHLIK, J. Org. Chem., 28 (1963) 2044.
6 L. H. STERNBACH AND S. KAISER, J. Am. Chem. Soc., 74 (1952) 2215.
7 HUANG-MINLON, J. Am. Chem. Soc., 68 (1946) 2487;
   G. R. CLEMO AND T. P. METCALFE, J. Chem. Soc., (1937) 1989.
8 J. JANAK, Ann. N.Y. Acad. Sci., 72 (1959) 606.
9 E. CREMER AND F. PRIOR, Z. Elektrochem., 55 (1951) 66.
10 A. T. JAMES AND A. J. P. MARTIN, J. Appl. Chem. (London), 6 (1956) 105.
11 R. F. CURTIS AND G. T. PHILLIPS, J. Chromatog., 9 (1962) 366.
12 H. PINES AND W. O. HAAG, J. Am. Chem. Soc., 82 (1960) 2471;
   H. PINES AND C. N. PILLAI, J. Am. Chem. Soc., 82 (1960) 2401; 83 (1961) 3270, 3274.
13 S. A. GREENE AND H. PUST, J. Phys. Chem., 62 (1958) 55.