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Note

High-performance liquid chromatography of adamantanones and other cyclic ketones

L. VODIČKA*, D. PRŮŠOVÁ, J. KRÍŽ and J. BURKHARD

Institute of Chemical Technology, Laboratory of Synthetic Fuels, Suchbátarova 5, 166 28 Prague 6 (Czechoslovakia)

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In this study the liquid chromatographic behaviour of some monocyclic and polycyclic ketones is investigated on a silica gel stationary phase with twelve mobile phases, containing *n*-heptane, diethyl ether and 2-propanol. A closely related study of the chromatographic behaviour of polycyclic alcohols (mostly adamantane derivatives) was performed under nearly identical experimental conditions¹.

EXPERIMENTAL

Apparatus

A Varian 8500 liquid chromatograph with a syringe pump was used, connected to a refractive index detector and A25 dual-channel strip-chart recorder (Varian, Palo Alto, CA, U.S.A.). Sample injection was performed using the stop-flow technique, with 5- and 10- μ l syringes (Hamilton, Bonaduz, Switzerland). The column was a Micropak Si-10 (50 cm \times 2 mm I.D., Varian) packed with 10- μ m LiChrosorb Si 60 silica gel.

Retention data were calculated on an HP 9830A calculator connected with an HP 9866A thermal printer (Hewlett-Packard, Avondale, PA, U.S.A.).

Monocyclic ketones were kindly provided by the Department of Organic Technology, Prague Institute of Chemical Technology. Polycyclic ketones were prepared in our Laboratory. Purification procedures for the solvents used as mobile phases have been described previously¹.

Mobile phases

The following mobile phases were prepared by weighting from degassed components: *n*-heptane–2-propanol; *n*-heptane–diethyl ether; *n*-heptane–diethyl ether–2-propanol. Exact compositions for the nine phases used are given in Table I.

Procedure

Retention data of monocyclic and polycyclic ketones together with those of polycyclic alcohols were measured according to the procedure described earlier¹.

TABLE I
MOBILE PHASE COMPOSITION (% w/w)

<i>n</i> -Heptane	2-Propanol
99	1
98	2
97	3
<i>n</i> -Heptane	Diethyl ether
65	35
50	50
35	65
<i>n</i> -Heptane-diethyl ether (65:35)	2-Propanol
99.9	0.1
99.5	0.5
99.0	1.0

RESULTS AND DISCUSSION

The values of retention time (t_R) and of the capacity factor (k') are given in Tables II-IV. In the case of ketones, it proved impossible to use mobile phases containing chloroform. Either the retention times were too short, or the peaks corresponding to the compounds investigated interfered with the so-called vacant peaks², which are sometimes observed when using a differential refractometer or another universal detector. Generally, ketones are eluted more rapidly than alcohols, the former being less polar³. This behaviour was also observed for the ketones investigated in the present study, ketones always being eluted before the corresponding alcohols, e.g., adamantanone before adamantan-2-ol, diamantanone before diamantan-3-ol,

TABLE II
RETENTION DATA

Mobile phase: $a\%$ *n*-heptane + $b\%$ 2-propanol. C = Number of carbon atoms; t_R = retention time (sec); k' = capacity factor.

Compound	C	$a = 99, b = 1$		$a = 98, b = 2$		$a = 97, b = 3$	
		t_R	k'	t_R	k'	t_R	k'
Cyclohexanone	6	504	2.11	385	1.38	341	1.10
Cyclopentanone	5	638	2.94	424	1.61	384	1.37
Cyclooctanone	8	444	1.74	343	1.12	300	0.85
2-Methylcyclohexanone	7	366	1.26	274	0.69	252	0.56
3-Methylcyclohexanone	7	431	1.66	326	1.01	290	0.79
4-Methylcyclohexanone	7	448	1.76	348	1.15	314	0.94
Bicyclo[3.3.1]nonan-2-one	9	428	1.64	325	1.01	288	0.78
Adamantanone	10	424	1.61	322	0.99	286	0.76
1-Methyladamantan-2-one	11	290	0.79	244	0.50	228	0.41
5-Methyladamantan-2-one	11	371	1.29	287	0.77	262	0.61
Diamantanone	14	372	1.30	289	0.79	258	0.59
Methyl adamant-1-yl ketone	11	290	0.79	252	0.56	238	0.47
Ethyl adamant-1-yl ketone	12	237	0.70	228	0.41	214	0.32
Propyl adamant-1-yl ketone	13	190	0.17	181	0.12	168	0.04
Methyl adamant-2-yl ketone	11	402	1.48	324	1.00	288	0.78

TABLE III

RETENTION DATA

Mobile phase: $a\%$ *n*-heptane + $b\%$ diethyl ether.

Compound	C	$a = 65, b = 35$		$a = 50, b = 50$		$a = 35, b = 65$	
		t_R	k'	t_R	k'	t_R	k'
Cyclohexanone	6	478	1.95	361	1.23	298	0.84
Cyclopentanone	5	498	2.07	388	1.39	336	1.07
Cyclooctanone	8	414	1.56	338	1.09	280	0.73
2-Methylcyclohexanone	7	298	0.84	242	0.50	226	0.39
3-Methylcyclohexanone	7	378	1.33	290	0.79	274	0.69
4-Methylcyclohexanone	7	412	1.54	310	0.91	277	0.71
Bicyclo[3.3.1]nonan-2-one	9	418	1.58	324	1.00	274	0.69
Adamantanone	10	384	1.37	305	0.88	266	0.64
1-Methyladamantan-2-one	11	264	0.63	226	0.39	203	0.25
5-Methyladamantan-2-one	11	340	1.10	274	0.69	242	0.50
Diamantanone	14	358	1.21	290	0.79	254	0.57
Methyl adamant-1-yl ketone	11	256	0.58	222	0.37	206	0.27
Ethyl adamant-1-yl ketone	12	268	0.65	222	0.37	208	0.28
Propyl adamant-1-yl ketone	13	180	0.11	170	0.05	172	0.06
Methyl adamant-2-yl ketone	11	396	1.44	312	0.93	264	0.63

TABLE IV

RETENTION DATA

Mobile phase: $a\%$ (65% *n*-heptane + 35% diethyl ether) + $b\%$ 2-propanol.

Compound	C	$a = 99.9, b = 0.1$		$a = 99.5, b = 0.5$		$a = 99.0, b = 1.0$	
		t_R	k'	t_R	k'	t_R	k'
Cyclohexanone	6	401	1.47	341	1.10	313	0.93
Cyclopentanone	5	449	1.77	360	1.22	324	1.00
Cyclooctanone	8	367	1.27	312	0.93	287	0.77
2-Methylcyclohexanone	7	276	0.70	243	0.52	194	0.20
3-Methylcyclohexanone	7	364	1.24	298	0.84	266	0.64
4-Methylcyclohexanone	7	359	1.21	314	0.94	278	0.72
Bicyclo[3.3.1]nonan-2-one	9	383	1.36	302	0.87	286	0.76
Adamantanone	10	361	1.23	308	0.90	276	0.70
1-Methyladamantan-2-one	11	250	0.54	226	0.39	212	0.31
5-Methyladamantan-2-one	11	310	0.91	266	0.64	244	0.50
Diamantanone	14	341	1.10	287	0.77	254	0.57
Methyl adamant-1-yl ketone	11	250	0.54	228	0.41	216	0.33
Ethyl adamant-1-yl ketone	12	256	0.58	226	0.39	216	0.33
Propyl adamant-1-yl ketone	13	180	0.11	178	0.10	173	0.07
Methyl adamant-2-yl ketone	11	370	1.28	310	0.91	276	0.70

1-methyladamantan-2-one before 1-methyladamantan-2-ol and cyclohexanone before cyclohexanol.

Structural effects

Retention times of compounds with one keto group decrease with increasing number of carbon atoms in the basic skeleton. The dependence of the logarithm of

the capacity factor on the number of carbon atoms in monocyclic and polycyclic ketones is shown in Fig. 1. Retention times decrease both with expanding ring size (for example in the series cyclopentanone, cyclohexanone, cyclooctanone) and with increasing the number of rings (bicyclononanone, adamantanone, diamantanone).

Fig. 2 is a chromatogram of some of the ketones, which can be separated on the basis of the differences in molecular size. The retention time of a cyclic ketone decreases after substitution with an alkyl group, becoming lower than that of the

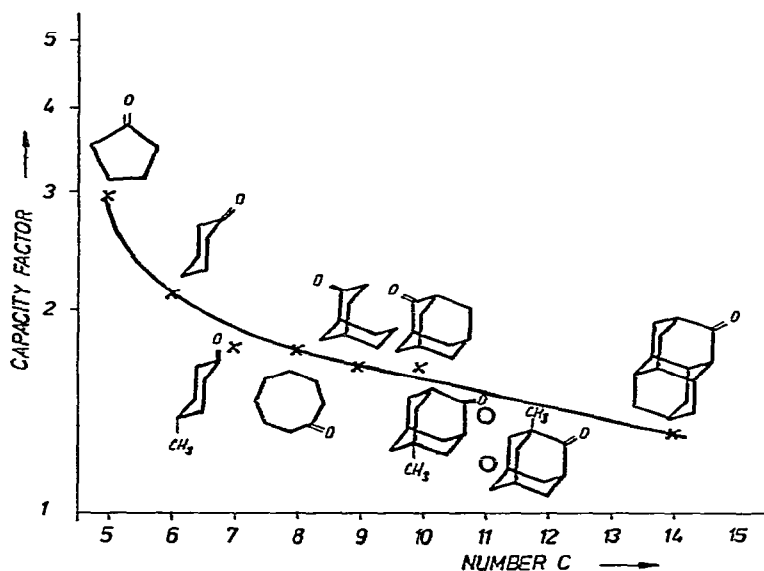


Fig. 1. Plot of capacity factor k' vs. the number of carbon atoms.

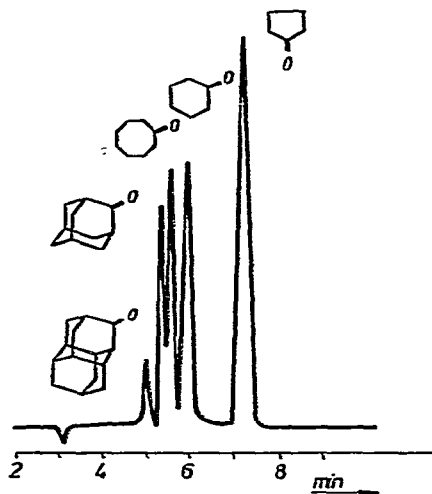


Fig. 2. Separation of the mixture of ketones. Column: MicroPak Si-10. Mobile phase: *n*-heptane-2-propanol (99:1); flow-rate, 30 ml/h.

analogous non-alkylated compound with the same number of carbons. This can be illustrated by 4-methylcyclohexanone, which has a lower retention time than the value estimated for cycloheptanone. Similarly, both methyladamantanones studied are eluted sooner than the time estimated for the corresponding polycyclic ketone.

The differences in retention times observed for the individual methyl ketones are caused by steric and/or other effects. 1-Methyladamantan-2-one is eluted faster than the isomeric 1-methyladamantan-4-one, the latter being less sterically hindered. A chromatogram of both these compounds is presented in Fig. 3.

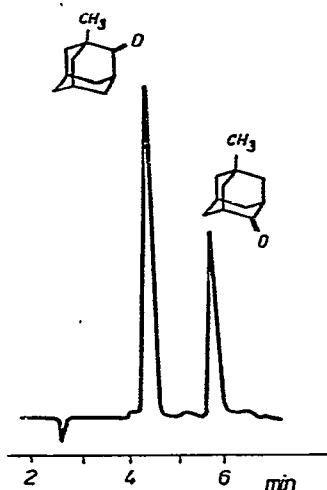


Fig. 3. Separation of methyladamantanones. Conditions as in Fig. 2.

Compounds with the keto group in a side chain (alkyl adamantyl ketones) are characterized generally by shorter elution times than ketones with the keto group in one of the rings of the molecule. On increasing the length of the alkyl group, the retention times decrease. It was observed for the two isomeric methyl adamantyl ketones that a stronger adsorption is exhibited by the isomer with the keto group bonded to a secondary carbon atom as compared with the isomer in which the keto group is on a tertiary carbon atom. Fig. 4 illustrates the separation of methyl adamantyl ketones.

Effect of mobile phase composition

As in the case of alcohols¹, for ketones there is a linear dependence of $\log k'$ on the logarithm of concentration of the more polar component in the mobile phase, as described by the Jandera⁴ equation

$$\log k' = A - n \log c$$

where c is the concentration of the more polar component in a two-component mobile phase, and n and A are constants.

Good agreement between experimental data and the above equation was observed when two-component mobile phases were used, *i.e.*, *n*-heptane-2-propanol

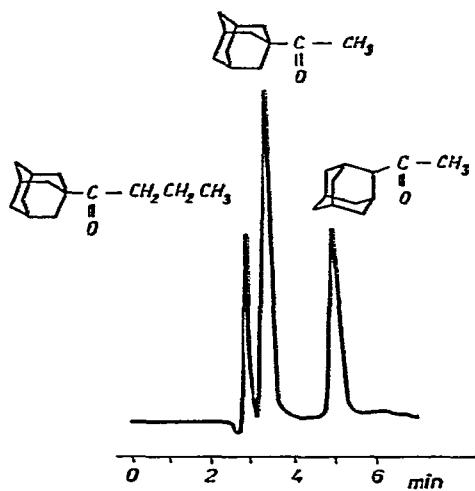


Fig. 4. Separation of alkyl adamantyl ketones. Conditions as in Fig. 2.

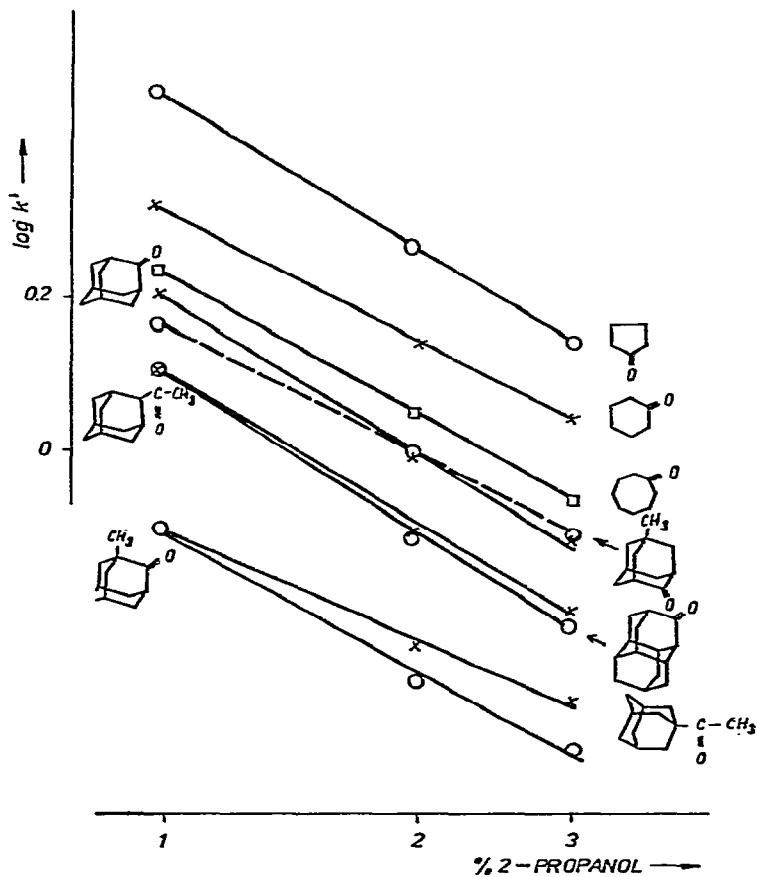


Fig. 5. Variation of the logarithm of the capacity factor with concentration of 2-propanol in the mobile phase *n*-heptane-2-propanol mixture).

and *n*-heptane–diethyl ether. Fig. 5 shows the dependence of $\log k'$ on the concentration of 2-propanol in the mobile phase for several ketones. A similar dependence has been found for elution data obtained in a three-component mobile phase (*n*-heptane–diethyl ether–2-propanol). However, here the quantity c expresses the concentration of the most polar component (*viz.*, 2-propanol), while the *n*-heptane–diethyl ether ratio was held constant.

The elution sequence of the compounds studied changes little with a change in the mobile phase composition. Some changes can be observed only in the differences between the retention times of the individual compounds. Fig. 6 shows the dependence of retention times of unsubstituted ketones on the mobile phase.

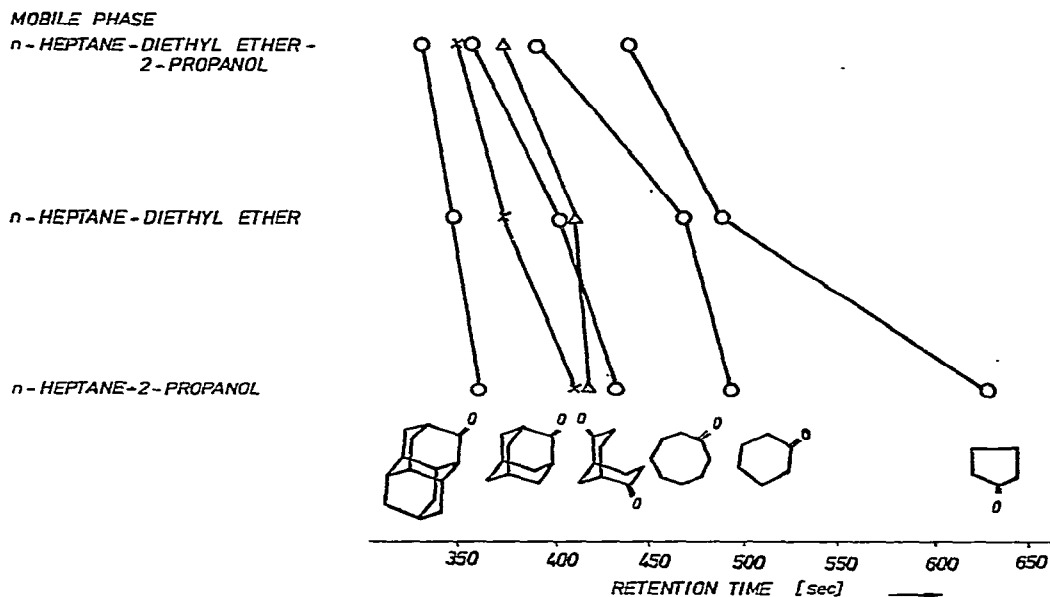


Fig. 6. Elution order of non-substituted cyclanones for three different mobile phases.

The compositions of the mobile phases used for measurements of ketone retention data were selected by reference to the previous measurements for alcohols¹. The separation of the ketones may be further improved by decreasing the elution strength of the mobile phases.

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