Acid-Catalyzed Hydrolysis of Bridged Bi- and Tricyclic Compounds. XXXI. Dependences on Temperature of α-Values in the Hydration of some Norbornenes

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Hydration rate constants of 2-norbornene and 5-methyl-*exo*- and *-endo*-5-hydroxymethyl-2-norbornenes were measured in aqueous perchloric acid solution at different acid concentrations and temperatures. Disappearance of 2-norbornene was followed spectrophotometrically and those of the substituted norbornenes by GLC. The excess acidity method was used to evaluate the α-values, which slightly decrease with rising temperature (7–16% within 50 K), provided that the slope parameter m^* is independent of temperature. In the case of 5-methyl-5-hydroxy-methyl-2-norbornenes the excess acidity plots, i.e. log k_a vs. X_0, were corrected according to the partial protonation of the hydroxyl oxygen atom.

The Brönsted catalysis law (1)[1] is an important equation,

$$k_{HA} = G(K_{HA})^x \tag{1}$$

e.g. in reaction-mechanistic studies and for estimation of reaction rates (k_{HA} = rate constant) under the catalysis of an acid HA (K_{HA} = dissociation constant) in aqueous solutions. G and α are parameters, of which α is much more important because it evidently indicates the position ($0 \leq \alpha \leq 1$) of the transition state between the initial and the final states of the rate-determining stage.[2] According to Brönsted,[1] G is a constant which is dependent on temperature, pressure, medium and substrate, and α (originally x) is a proper fraction which is reasonably assumed to be a continuous function of K_{HA} for acids of the same type. The dissociation constant K_{HA} often depends on temperature, pressure and medium; however, to our knowledge, the dependences of the parameter α on temperature, pressure and medium have never been measured.

This paper is concerned with the dependence of α on temperature. The parameter α can be measured by many different methods, which have recently been collated.[3] The temperature dependence of α has, however, been difficult and laborious to measure reliably, but the new excess acidity method provides an opportunity to attempt such a measurement.[4] In this method α ($= m^{\neq}$) is

$$\log k_\psi - \log c_{H^+} = m^{\neq} m^* X_0 + \log k_0 \tag{2}$$

obtained from the slope ($m^{\neq} m^*$) of the linear eqn. (2) by dividing the slope by a constant m^*-value (1.80 ± 0.10 if a carbon atom is protonated) which is independent of temperature.[5,6] The values of observed rate constants of the reaction (k_ψ), acid concentrations (c_{H^+}) and excess acidities (X_0) of the medium are dependent on temperature, but they are generally easy and accurate to measure or to calculate at different temperatures, e.g. by using eqn. (3).[4]

$$X_{0,T} = (298.15 \text{ K}/T) X_{0, 298.15 \text{ K}} \tag{3}$$

In order to see whether the excess acidity method gives sufficiently accurate values of α for mutual comparison at different temperatures, eqn. (2) has been applied to acid-catalyzed hydrations of 2-bicyclo[2.2.1]heptene or 2-norbornene (1) and 5-methyl-*exo*- and *-endo*-5-hydroxy-methyl-2-norbornenes (2 and 3), which reactions occur by the rate-determining protonation of the double bond (an A-S_E2 or Ad_E2 mechanism).[7–9]

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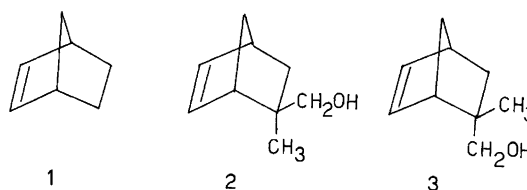
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Experimental

Materials. 2-Norbornene was a commercial product from Fluka AG (ca. 97%). It was purified by distillation

Table 1. Disappearance rate constants of 2-norbornene in aqueous perchloric acid solutions at different acid concentrations and temperatures.

T/K	$c(HClO_4)/^a$ mol dm^{-3}	X_0^b	$k_\psi/$ 10^{-4} s^{-1}
283.2	2.50	0.649	0.89(3)
	3.02	0.799	1.99(2)
	3.47	0.947	4.27(3)
	4.01	1.146	10.05(5)
	4.47	1.339	22.2(2)
	4.99	1.580	58.1(5)
	5.53	1.861	169(1)
293.2	2.04	0.514	1.67(8)
	2.49	0.627	3.16(6)
	3.01	0.771	7.78(3)
	3.46	0.915	15.5(2)
	4.00	1.107	36.8(2)
	4.47	1.293	82.6(5)
	4.98	1.526	201(11)
	5.52	1.798	512(10)
303.2	1.49	0.380	2.52(8)
	2.03	0.500	5.88(5)
	2.48	0.607	10.94(4)
	3.00	0.746	23.95(6)
	3.45	0.884	45.2(14)
	3.98	1.070	99.2(6)
	4.45	1.251	210(5)
	4.97	1.476	431(6)
313.2	0.505	0.144	1.17(15)
	1.037	0.269	4.98(7)
	1.48	0.368	9.68(9)
	2.03	0.484	20.9(3)
	2.47	0.587	38.0(7)
	2.99	0.722	74.0(4)
	3.43	0.856	127(3)
	3.97	1.036	228(1)
	4.43	1.211	463(6)
323.2	0.505	0.140	4.2(5)
	0.987	0.252	12.3(4)
	1.48	0.357	26.5(2)
	2.02	0.467	54.7(7)
	2.46	0.569	95.6(10)
	2.97	0.700	192(2)
	3.42	0.830	326(14)
	3.95	1.004	730(43)
333.2	0.502	0.136	12.0(6)
	0.746	0.193	20.7(11)
	0.981	0.245	33.6(17)
	1.47	0.347	69.7(14)
	1.95	0.444	128(2)
	2.45	0.555	236(14)
	2.96	0.682	435(4)
	3.40	0.809	783(47)

[a] Corrected according to temperature and to dilution caused by addition of the substrate as a methanol solution. [b] Excess acidity[5] corrected according to temperature [eqn. (3)].

through an efficient column (purity > 99.5% by GLC; b.p. 95.5–96°C at 100 kPa). A mixture of 5-methyl-5-hydroxymethyl-2-norbornenes was obtained by reduction with lithium aluminium hydride of the product of the Diels–Alder reaction between monomerized cyclopentadiene and methacrolein.[9] It was purified by distillation (purity ca. 99% by GLC) and used as mixtures, the *exo/endo* ratio of which varied between 6/1 and 3/1.

Kinetic measurements. The disappearance of 2-norbornene in aqueous perchloric acid solutions was monitored on a Cary 17 D spectrophotometer by a method

Table 2. Disappearance rate constants of 5-methyl-*exo*- and -*endo*-5-hydroxymethyl-2-norbornenes (2 and 3) in aqueous perchloric acid solutions at different acid concentrations and temperatures.

T/K	$c(HClO_4)/^a$ mol dm^{-3}	X_0^b	$k_\psi(2)/$ 10^{-4} s^{-1}	$k_\psi(3)/$ 10^{-4} s^{-1}
283.2	2.04	0.533	0.0407(14)	0.069(3)
	2.40	0.625	0.0556(25)	0.096(2)
	3.03	0.790	0.143(10)	0.220(8)
	3.40	0.915	0.248(5)	0.383(7)
	4.03	1.140	0.725(15)	0.881(14)
	4.32	1.258	1.06(3)	1.32(5)
	5.07	1.613	3.33(5)	3.57(5)
	5.43	1.778	5.99(18)	6.13(17)
298.2	1.38	0.359	0.118(11)	0.210(8)
	2.03	0.503	0.287(8)	0.487(10)
	2.39	0.594	0.482(11)	0.744(13)
	3.02	0.751	1.19(2)	1.70(2)
	3.39	0.869	2.52(5)	3.17(3)
	4.01	1.082	6.10(26)	7.05(24)
	4.30	1.195	9.79(14)	10.98(23)
	5.06	1.532	23.0(6)	24.3(11)
	5.41	1.688	39.2(6)	38.3(4)
313.2	1.37	0.341	0.735(24)	1.20(2)
	2.02	0.479	2.10(2)	3.14(6)
	2.37	0.562	3.13(9)	4.47(12)
	3.00	0.711	7.82(5)	10.06(20)
	3.37	0.823	12.5(2)	15.6(2)
	3.99	1.030	29.2(8)	32.4(10)
	4.28	1.138	39.9(14)	44.4(12)
	5.03	1.458	121(2)	120(2)
328.2	0.500	0.138	0.908(8)	1.47(3)
	1.000	0.250	2.67(4)	4.08(6)
	1.36	0.326	4.86(6)	7.26(10)
	2.01	0.457	12.2(1)	17.1(4)
	2.36	0.540	18.5(3)	24.9(4)
	2.97	0.682	39.0(7)	48.1(17)
	3.34	0.790	63.0(10)	75.8(22)
343.2	0.500	0.132	4.47(8)	7.32(18)
	0.742	0.186	8.25(4)	12.76(4)
	0.976	0.237	12.37(9)	18.14(16)
	1.46	0.336	26.9(1)	37.5(3)
	1.99	0.442	55.0(5)	73.4(8)
	2.43	0.537	90.6(6)	119.1(6)

[a] Corrected according to temperature and to dilution caused by addition of the substrate and the internal standard. [b] Excess acidity[5] corrected according to temperature [eqn. (3)].
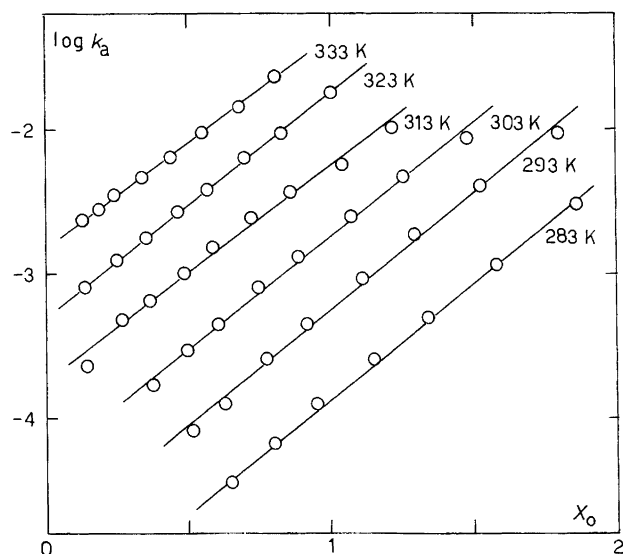
Fig. 1. Excess acidity plots for the acid-catalyzed hydration of 2-norbornene in $HClO_4$(aq) at different temperatures. The rate constants $(k_a = k_\psi/c_{H^+})$ and excess acidities (X_0) are from Table 1. The straight lines have been calculated by using eqn. (2).

described earlier.[10] The disappearance of both exo- and endo-isomers of 5-methyl-5-hydroxymethyl-2-norbornene in aqueous perchloric acid solutions was followed simultaneously by taking samples after appropriate intervals, by extracting them quickly with methylene chloride and by analyzing the organic solutions on a Perkin Elmer Autosystem gas chromatograph employing an SE-30 or FFAP capillary column. 3-Nitrotoluene was used as

internal standard in the former case and nitrobenzene in the latter case.

The disappearance rates always followed strictly first-order kinetics, and the rate constants were calculated from the slope of the linear correlation $\ln(A_t - A_\infty)$ vs. t, where A is an absorbance in the spectrophotometric measurements and a ratio of the integrals of the substrate and the internal standard in the GLC measurements. Each rate constant was measured at least twice.

Results and discussion

The disappearance rate constants of 2-norbornene (1) in aqueous perchloric acid solutions at different acid concentrations and temperatures are listed in Table 1, and the corresponding data for 5-methyl-exo- and -endo-5-hydroxymethyl-2-norbornenes (2 and 3) are presented in Table 2. The values are in good agreement with the rate constants measured earlier.[8-10] The products of the reactions have been studied earlier.[8,9,11]

The data in Table 1 are fitted by employing eqn. (2) to obtain values for the slope parameter $m^{\neq} m^*$, and the slopes are divided by m^* ($= 1.80$)[5,6] to obtain values for $m^{\neq}$ or x (the so-called excess acidity x)[3] at six temperatures. The plots of $\log k_a$ vs. X_0 ($k_a = k_\psi/c_{H^+}$) are almost linear (Fig. 1; $r = 0.998$ on average), although a slight, unexpected downward curvature can be seen at several temperatures. The reason for this curvature is unknown and requires further study. The slopes and α-values are presented in Table 3. The α-values are between 0.82 and 0.90 and possibly show a slightly decreasing trend with rising temperature: $\alpha = -(1.2 \pm 0.5) \times 10^{-3}$ $K + (1.24 \pm 0.17)$. The change is only ca. 7% within a

Table 3. The parameters of eqn. (2) for 2-norbonene (1) and of eqn. (4) for 5-methyl-exo- and -endo-5-hydroxymethyl-2-norbornene (2 and 3) in the hydration in aqueous perchloric acid solutions at different temperatures.

Substrate	T/K	$m^{\neq} m^*$	α^a	$\log k_0^b$	r^c
1	283.2	1.59(3)	0.88(2)	$-5.44(3)$	0.9993
	293.2	1.61(5)	0.90(3)	$-4.86(5)$	0.997
	303.2	1.57(5)	0.87(3)	$-4.31(4)$	0.997
	313.2	1.50(6)	0.83(3)	$-3.74(4)$	0.994
	323.2	1.56(1)	0.87(1)	$-3.30(1)$	0.9998
	333.2	1.47(1)	0.82(1)	$-2.83(1)$	0.9998
2	283.2	1.89(3)	1.05(2)	$-6.74(4)$	0.9992
	298.2	1.94(4)?	1.08(2)?	$-5.77(4)$?	0.998
	298.2	$1.87(4)^d$	$1.04(4)^d$	$-5.73(4)^d$	0.998^d
	313.2	1.79(2)	0.99(1)	$-4.84(2)$	0.9996
	328.2	1.67(2)	0.93(1)	$-3.97(1)$	0.9997
	343.2	1.62(3)	0.90(2)	$-3.26(1)$	0.9993
3	283.2	1.69(1)	0.94(2)	$-6.40(3)$	0.9993
	298.2	1.68(3)	0.93(2)	$-5.43(3)$	0.9991
	313.2	1.59(2)	0.88(1)	$-4.57(2)$	0.9997
	328.2	1.46(2)	0.81(1)	$-3.74(1)$	0.9995
	343.2	1.38(5)	0.77(3)	$-3.03(2)$	0.997
	343.2	$1.39(5)^d$	$0.77(3)^d$	$-3.03(2)^d$	0.997^d

$^a \alpha = m^{\neq} = m^{\neq} m^*/1.80$; the divisor is fixed to be exact in estimation of the error limits. $^b k_0$ in dm^3 mol^{-1} s^{-1}. ^{c}A correlation coefficient of a linear plot [eqn. (2) for 1 and eqn. (4) for 2 and 3]. ^{d}With parameter values $m' = 1.00$ and $K_{S \cdot H^+} = 100$ mol dm^{-3} (cf. Table 4).

range of 50 K and is thus of the order of experimental scatter. The present α-values are in satisfactory agreement with that (0.79 ± 0.04) measured earlier by GLC for the acid-catalyzed hydration of norbornene at 298 K.[3,8]

In the hydration of the isomeric 5-methyl-5-hydroxymethyl-2-norbornenes the plots of log k_a vs. X_0 (Table 2) are slightly curved at all five temperatures used (Figs. 2 and 3). A probable reason for the curvature in this case is a fast protonation of the hydroxyl oxygen atom in addition to the slow protonation of an olefinic carbon atom. The pK_{SH^+} value of primary alcohols is -2.0, and thus they are half-protonated in ca. 4.4 mol dm^{-3} $HClO_4(aq)$.[12] The protonation equilibrium can be taken into account in the excess acidity method by adding a

$$\log k_a - \log [c_S/(c_S + c_{S'H^+})] = m^{\neq}m^*X_0 + \log k_0 \qquad (4)$$

correction term to eqn. (2), so that it takes the form of eqn. (4). This is in agreement with the approximation that the oxygen-protonated substrate $S'H^+$ is not protonated further on an olefinic carbon atom (Scheme 1). The correction term can be evaluated by the excess acidity method [eqn. (5)].[4]

$$\log (c_{S'H^+}/c_S) - \log c_{H^+} = m'X_0 + pK_{S'H^+} \qquad (5)$$

Eqns. (4) and (5) can be used in two different ways: one method is to fix m' and p $K_{S'H^+}$ to probable values and to use them to calculate the correction term; the other is to let their values vary and use a nonlinear least-squares minimization to fit the experimental log k_a values vs. X_0
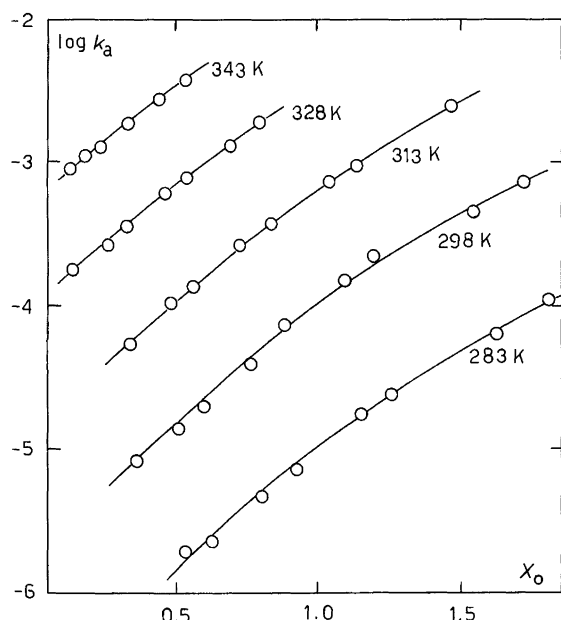

Fig. 2. Excess acidity plots for the acid-catalyzed hydration of 5-methyl-exo-5-hydroxymethyl-2-norbornene in $HClO_4(aq)$ at different temperatures. The rate constants $(k_a = k_\psi/c_{H^+})$ and excess acidities (X_0) are from Table 2. The curves have been calculated by using eqn. (6).
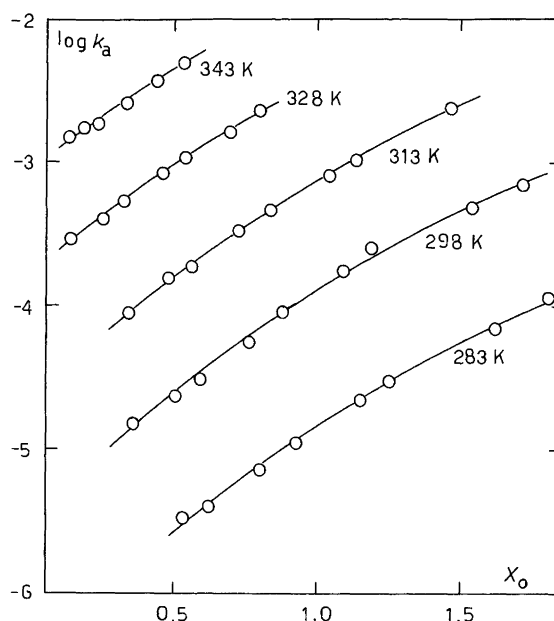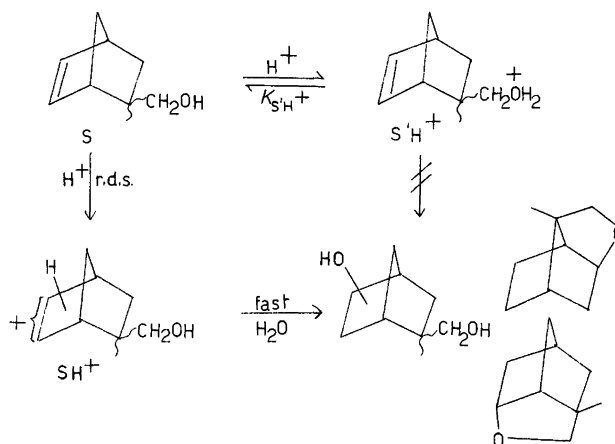

Fig. 3. Excess acidity plots for the acid-catalyzed hydration of 5-methyl-endo-5-hydroxymethyl-2-norbornene in $HClO_4(aq)$ at different temperatures. The rate constants $(k_a = k_\psi/c_{H^+})$ and excess acidities (X_0) are from Table 2. The curves have been calculated by using eqn. (6).

Scheme 1.

and c_{H^+} via eqn. (6), which is a combination of eqns. (4) and (5). The latter method, however, demands rather well

$$\log k_a = m^{\neq}m^*X_0 - \log [1 + (c_{H^+}/K_{S'H^+})10^{m'X_0}]$$
$$+ \log k_0 \qquad (6)$$

guessed initial values for $m^{\neq}m^*$, $K_{S'H^-}$, m' and log k_0, because there are several minima where an iteration can be ended owing to the complexity of eqn. (6). The evaluated values for $m^{\neq}m^*$ and log k_0 are listed in Table 3, together with the calculated α-values. The values for $K_{S'H^+}$ and m' are given in Table 4.

The evaluated $K_{S'H^-}$ (or $pK_{S'H^-}$) values are similar to those $(pK_{S'H^+} = -1.99 \pm 0.04)$[12] measured for the proto-

Table 4. The values of $K_{S'H^+}$, p$K_{S'H^+}$ and m' evaluated by iteration with eqn. (6) for the hydration of 5-methyl-exo- and -endo-5-hydroxymethyl-2-norbornene (2 and 3) at different temperatures.

Substrate	T/K	$K_{S'H^+}$/mol dm^{-3}	p$K_{S'H^+}$	m'
2	283.2	100	-2.00	0.99
	298.2	109	-2.04	1.10
	313.2	98	-1.99	1.01
	328.2	100	-2.00	1.04
	343.2	100	-2.00	1.00
	Av.	101 (4)	-2.01 (2)	1.03 (4)
3	283.2	95	-1.98	0.97
	298.2	118	-2.07	1.05
	313.2	100	-2.00	0.99
	328.2	100	-2.00	1.01
	343.2	78	-1.89	0.73
	Av.	98(15)	-1.99(7)	1.01(3)[a]

[a] The value 0.73 is excluded.

nation of methanol and ethanol in aqueous sulfuric acid between 298 and 333 K, and are practically independent of temperature, as are also the values for methanol and ethanol. The m'-values are close to unity (1.02 ± 0.04), as has recently been observed in the case of the protonation of the ether oxygen atom of several alkyl phenyl ethers in aqueous perchloric acid (m' = 0.98 ± 0.03);[13] neither do they show any dependence on temperature, which supports the temperature independence of m^*.

The calculated values of α are between 0.90 and 1.05 in the case of the exo isomer and between 0.77 and 0.94 in the case of the endo isomer, and show a clearer decreasing trend with rising temperature than those of 2-norbornene (see above). The change is ca. 15–20% within the range of 60 K (or 13–16% within 50 K), and is thus probably more than experimental scatter. The present values are greater than those (0.79 ± 0.01 for the exo and 0.49 ± 0.01 for the endo isomer at 348 K) measured earlier by the isotopic fractionation method, although the present α(endo) value (0.77 at 343 K) agrees well with the older α(exo) value at 348 K.[9] The older α(endo) value is evidently false, as has been suspected.[3]

The present α(exo) values are steadily greater (13 ± 2%) than the α(endo) values (Table 3). A possible reason is the location of the hydroxyl group in the case of the exo isomer far from the reaction center of protonation of the double bond. Thus the protonation of the

hydroxyl oxygen perhaps does not totally prevent the protonation of an olefinic carbon, as expected from Scheme 1. This might also be a reason for the unusually high α(exo) values. Another possible reason is an (at least partial) endo protonation of the double bond in the case of the endo isomer via the protonated 5-hydroxymethyl group, which is situated in an excellent position to transfer a proton to an olefinic carbon atom. There is already a weak hydrogen bond between the unprotonated endo-5-hydroxymethyl group and the double bond.[14] The hydration rate of the endo isomer is generally greater than that of the exo isomer, although the difference decreases with the increasing acid concentration and the rising temperature (Table 2). The protonated endo-5-hydroxymethyl substituent should, however, retard the protonation of the double bond from the exo side by a field effect much more effectively than the protonated exo-5-substituent. More investigations are needed.

References

1. Brönsted, J. N. Chem. Rev. 5 (1928) 231.
2. e.g. Kresge, A. J. In: Caldin, E. and Gold, V., Eds., Proton Transfer Reactions, Chapman and Hall, London 1975, pp. 179–199.
3. Lajunen, M. Acta Chem. Scand. 45 (1991) 377.
4. Cox, R. A. Acc. Chem. Res. 20 (1987) 27.
5. Cox, R. A. and Yates, K. Can. J. Chem. 59 (1981) 2116.
6. Cox, R. A. and Yates, K. Can. J. Chem. 62 (1984) 2155.
7. Chwang, W. K., Nowlan, V. J. and Tidwell, T. T. J. Am. Chem. Soc. 99 (1977) 7233.
8. Lajunen, M. and Hirvonen, P. Finn. Chem. Lett. (1978) 38.
9. Lajunen, M. and Peuravuori, J. Finn. Chem. Lett. (1976) 99.
10. Allen, A. D. and Tidwell, T. T. J. Am. Chem. Soc. 104 (1982) 3145.
11. Kablaoui, M. S. Ph.D. Thesis, University of South Carolina 1967.
12. Perdoncin, G. and Scorrano, G. J. Am. Chem. Soc. 99 (1977) 6983.
13. Lajunen, M. and Kähkönen, M. Acta Chem. Scand. 46 (1992) 726.
14. Jalonen, J. and Taskinen, J. J. Chem. Soc., Perkin Trans. 2 (1985) 1833.