THE SEARCH FOR THE ACTIVE BASE OPERATING IN ALKOXIDE PROMOTED E2 REACTIONS IN LOW POLAR SOLVENTS: A KINETIC ANALYSIS OF THE ELUSIVE PROBLEM*

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Received May 27th, 1981

Partial kinetic orders in base for 1-decene, *cis*-2-decene and *trans*-2-decene formation from the reaction of 2-decyl bromide with t-C_4H_9OK in tetrahydrofuran and in tert-butanol and with t-C_4H_9ONa in tert-butanol have been determined and their significance for assessment of active base has been probed. It has been ascertained that assessment of active base in alkoxide promoted E2 reactions is model-dependent. An unambiguous evidence has been provided by a kinetic analysis of the effect of base concentration on olefin-isomer distribution in the reaction. Two alternative kinetic models of this effect have been devised, the one assuming a competition of several active base species for a single substrate and the other a competition between an uncomplexed and alkoxide-complexed substrate for a single active base. Compatibility of both kinetic models with experimental data has been demonstrated.

In low polar solvents, selectivity of metal alkoxide-promoted eliminations from alkyl halides and tosylates is remarkably anomalous[1]. Contrary to a simple expectation, distribution of olefin-isomers in the reaction is concentration-dependent. Proportion of *cis*- and terminal alkenes increases markedly with increasing concentration of base[2,3]. At high alkoxide concentrations, prevalence of the less stable isomers is frequently observed[1].

According to the prevailing opinion[2,4,5], a concentration-dependent competition of several active base species differing in selectivity and in ionic association is responsible for such anomalous results. Various models of associated (ion-paired[6] or ion-aggregated[7,8]) base endowed with a "contrathermodynamic" propensity for *cis*- and terminal alkene formation have been proposed. Recently, however, another explanation[3] has been suggested, namely that concentration-dependent solvation of a substrate by metal alkoxide is responsible for orientational changes in the reaction.

In this paper the two alternative concepts are kinetically probed in the reaction of 2-decyl bromide with t-C_4H_9OK in tetrahydrofuran (THF) and in tert-butanol

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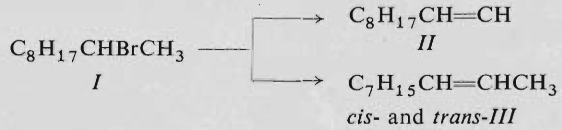
* Part XLV in the series Elimination Reactions; Part XLIV: This Journal *46*, 2166 (1981)

and with t-C_4H_9ONa in tert-butanol (Scheme 1). Overall rates, and also partial rates of the individual olefin-isomer formation have been determined at four different base concentrations in each of these reactions. Kinetic models respectively describing base species competition and solvation of substrate by metal alkoxide have been devised. Compatibility of the experimental data with the two alternative models has been examined.



SCHEME 1

EXPERIMENTAL

Materials

2-Decyl bromide was prepared as described previously[10]. The purity was checked by gas-chromatography (>98%). Tert-butanol was refluxed over calcium hydride and distilled twice with potassium metal. Tetrahydrofuran (Fluka; puriss.) was distilled with sodium metal before use. The solvents contained less than 0·003% (0·002 mol l^{-1}) of water (K. Fisher). Stock solutions of potassium and sodium tert-butoxide in tert-butanol (0·7 and 0·6 mol l^{-1}, respectively) were prepared by dissolving metal under reflux in tert-butanol. A stock solution of potassium tert-butoxide in tetrahydrofuran was prepared analogously by a treatment of potassium metal (20% excess) with a known amount of tert-butanol dissolved in tetrahydrofuran (with stirring at reflux temperature under nitrogen). Solutions employed in the kinetic study were obtained from the stock solutions by a dilution and the concentration was checked titrimetrically.

Kinetic Procedure

The rates of the elimination were measured gas-chromatographically from changes in concentration of the reaction products with time using the method of internal standard.

Determination of products and overall reaction rates: 2-Decyl bromide (44 mg; 0·2 mmol) and n-decane (internal standard; 10 mg) were mixed with 15—30 ml of the appropriate alkoxide solution in a rubber septum-capped flask immersed in the thermostatized bath. In known intervals aliquots were withdrawn (1—3 ml) by a syringe and quenched by a treatment with brine (25 ml) and pentane (1 ml) in 50 ml volumetric flask. The volumes were made up with water, shaken, and samples of the pentane layer were injected into gas-chromatograph. Gas-chromatography was performed on the Carlo Erba Fractovap GT apparatus equipped with a digital integrator under conditions described previously[9].

Evaluation of rate coefficients: The elimination was carried out in a large excess of the alkoxide so that it can be treated as a pseudomonomolecular process for which holds

$$k_1 = k_{n+1}[B]^n = \frac{1}{t}\ln\frac{R_\infty - R_0}{R_\infty - R_t}, \qquad (1)$$

where k_1 and k_{n+1} are rate coefficients, [B] is overall base concentration determined titrimetrically, n is the kinetic order in base in the reaction (*cf.* Discussion) and R_t, R_0 and R_∞ are ratios of the integrated areas corresponding to the sum of elimination products and to the internal standard, respectively, determined at time t (R_t), at the beginning of the measurement (R_0) and at the end of the reaction (R_∞). In order to avoid necessity of determination of R_0 and R_∞, and the experimental errors involved, the Eq. (*1*) was rewritten as

$$R_t = R_\infty - (R_\infty - R_0)\exp(-k_1 t) \qquad (2)$$

and R_∞ and $(R_\infty - R_0)$ were treated together with k_1 as unknown parameters. The experimental values R_t were fitted to the exponential curve (*2*). Spath's algorithm[11] was used for the simultaneous determination of the parameters R_∞, $(R_\infty - R_0)$ and k_1. The transcendent equation in this algorithm was solved by the standard regula falsi procedure[12]. The calculated values of k_1 for the reaction of 2-decyl bromide with t-C_4H_9OK in tetrahydrofuran and in tert-butanol, and with t-C_4H_9ONa in tert-butanol are summarized in Table I. The partial rate constants of the individual olefin-isomer formation, k_{E2}^p, were calculated from the equation

$$k_{E2}^p = (\%\,p)\,k_1/100, \qquad (3)$$

TABLE I

Rate coefficients k_1 (in s^{-1}) determined in alkoxide promoted eliminations from *I* at several base concentrations

Base/Solvent/Temp.	[Base][a] k_1	k_1[b]
t-C_4H_9OK/THF[c]/20°C	1·00	$(1.32 \pm 0.08) \cdot 10^{-3}$
	0·50	$(9.53 \pm 0.41) \cdot 10^{-4}$
	0·25	$(7.65 \pm 0.32) \cdot 10^{-4}$
	0·10	$(5.15 \pm 0.23) \cdot 10^{-4}$
t-C_4H_9OK/t-C_4H_9OH/80°C	0·67	$(5.45 \pm 0.19) \cdot 10^{-4}$
	0·33	$(2.04 \pm 0.03) \cdot 10^{-4}$
	0·16	$(1.03 \pm 0.03) \cdot 10^{-4}$
	0·07	$(3.92 \pm 0.12) \cdot 10^{-5}$
t-C_4H_9ONa/t-C_4H_9OH/80°C	0·51	$(8.08 \pm 0.20) \cdot 10^{-5}$
	0·26	$(5.23 \pm 0.13) \cdot 10^{-5}$
	0·13	$(2.70 \pm 0.09) \cdot 10^{-5}$
	0·05	$(1.27 \pm 0.10) \cdot 10^{-5}$

[a] Titrimetrical concentration (in mol l^{-1}). [b] Mean value and standard mean deviation based on 16—25 samples from two kinetic runs followed up to completion. [c] Tetrahydrofuran.

where (% p) is the percentage of the given isomer in the resulting olefin mixture. The requisite olefin-isomer composition data were determined by gas chromatography and are summarized in Table II.

TABLE II

Olefin-isomer composition in the kinetic runs

[Base][a]	% 1-Decene[b]	% *trans*-2-Decene[b]	% *cis*-2-Decene[b]
	Tert-C_4H_9OK–tetrahydrofuran (20°C)		
1·00	56·05 ± 0·38	33·34 ± 0·21	10·61 ± 0·17
0·50	54·62 ± 0·17	35·78 ± 0·25	9·60 ± 0·16
0·25	52·86 ± 0·25	38·19 ± 0·12	8·85 ± 0·48
0·10	51·88 ± 0·31	39·52 ± 0·17	8·60 ± 0·26
	Tert-C_4H_9OK–tert-butanol (80°C)		
0·67	79·14 ± 0·20	10·67 ± 0·18	10·19 ± 0·10
0·33	76·21 ± 0·12	12·77 ± 0·12	11·02 ± 0·08
0·16	75·24 ± 0·29	13·75 ± 0·19	11·01 ± 0·21
0·07	74·47 ± 0·20	14·22 ± 0·17	11·31 ± 0·20
	Tert-C_4H_9ONa–tert-butanol (80°C)		
0·51	76·27 ± 0·66	12·36 ± 0·62	11·37 ± 0·26
0·26	74·12 ± 0·93	14·59 ± 0·79	11·29 ± 0·60
0·13	73·01 ± 0·63	15·27 ± 0·59	11·72 ± 0·33
0·05	70·46 ± 1·18	17·42 ± 0·95	12·12 ± 0·40

[a] Titrimetrical concentration (in mol l^{-1}). [b] Mean value and standard mean deviation based on 16—25 samples from two kinetic runs followed up to completion.

RESULTS AND DISCUSSION

Dominant and Active Base Species in Alkoxide Promoted Reactions

As results of ebulliometric, thermoelectric and cryoscopic studies concordantly show, association of oppositely charged ions of alkali alkoxides to form ion pairs and/or ion pair aggregates,

$$\overset{+}{M} + \overset{-}{O}R \rightleftharpoons (\overset{+}{M}\overset{-}{O}R) \rightleftharpoons (\overset{+}{M}\overset{-}{O}R)_n\,, \quad n > 1\,, \qquad (A)$$

is a ubiquitous phenomenon in 0·05 – 1·0 mol l^{-1} solutions. In aprotic solvents of low polarity ion pair aggregates generally prevail[13,14]. For example, t-C_4H_9OK is a tetramer in tetrahydrofuran and in benzene, and t-C_4H_9ONa and t-C_4H_9OLi range from a tetramer in the former to an octamer in the latter solvent. Even in very polar (dipolar) aprotic solvents, aggregates of ion pairs sometimes predominate: in dimethyl sulphoxide, t-C_4H_9OK ranges between dimer and trimer and t-C_4H_9OLi is a tetramer[14]. In protic solvents, in a marked contrast, alkali alkoxides are usually monomeric ion pairs. As our recent study showed[15], *t*-C_4H_9OK and t-C_4H_9ONa in tert-butanol are simple ion pairs; only t-C_4H_9OLi forms aggregates. Predominance of ion-pair monomers is observed[16] also in the combinations i-C_3H_7OK–i-C_3H_7OH, i-C_3H_7ONa–i-C_4H_7OH, n-C_3H_7OK–n-C_3H_7OH, n-C_3H_7ONa–n-C_3H_7OH and n-C_3H_7OLi–n-C_3H_7OH. A substantial dissociation of metal alkoxides occurs only in the most polar protic solvents;[16,17] according to conductometric[17] studies 1M-C_2H_5ONa in ethanol still contains less than 20% of the dissociated ions.

When the dominant alkoxide species in a given reaction medium is known, the active species can be, in principle, assessed experimentally. Inevitably, however, some additional assumptions have to be made. Customarily, an assumption has been made that there is only one active base species in a given reaction and that equilibrium between the active species A and the dominant species D

$$d\,\mathrm{D} \overset{K}{\rightleftarrows} a\,\mathrm{A}\,, \qquad (B)$$

where *a* and *d* are stoichiometric coefficients for A and D, respectively, and *K* is the equilibrium constant, is rapid compared to the rate of the investigated reaction For the velocity of the reaction of substrate S then holds

$$v = k[\mathrm{A}]\,[\mathrm{S}]\,. \qquad (4)$$

Since for [A] holds

$$[\mathrm{A}] = K^{1/a}\,[\mathrm{D}]^{d/a} \approx K^{1/a}\,[\mathrm{ROM_t}]^{d/a}\,, \qquad (5)$$

where [$\mathrm{ROM_t}$]is the overall (titrimetrical) concentration of the alkoxide base, the Eq. (*4*) can be rewritten as

$$v = k'[\mathrm{ROM_t}]^{d/a}\,[\mathrm{S}] \qquad (6)$$

and the active base species can be accordingly assessed from the experimentally determined value of *d*/*a*, *i.e.*, from the apparent kinetic order in base in the investigated reaction.

The apparent kinetic orders in base we have determined in the reaction of 2-decyl bromide with t-C_4H_9OK–THF, t-C_4H_9OK–t-C_4H_9OH and t-C_4H_9ONa–t-C_4H_9OH

base–solvent systems are presented in Table III. Theoretical values of *d*/*a* expected for different combinations of active and dominant base species are in Table IV.

TABLE III

Kinetic order in base determined for the overall elimination from 2-decyl bromide

Base/Solvent	Kinetic order[a]
tert-C_4H_9OK/THF[b]	0·40 ± 0·02
tert-C_4H_9OK/tert-C_4H_9OH	1·14 ± 0·06
tert-C_4H_9ONa/tert-C_4H_9ONa	0·83 ± 0·04

[a] Mean values and standard mean deviations. [b] Tetrahydrofuran.

TABLE IV

Theoretical kinetic orders in base, *d*/*a*, expected for different pairs of active and dominant alkoxide species

Active base[a]	Dominant base				
	(B)[b]	(BM)	(B_2M)[c]	$(BM)_2$	$(BM)_4$
(B)[b]	1	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{4}$	$\frac{1}{8}$
(BM)	2	1	$\frac{2}{3}$	$\frac{1}{2}$	$\frac{1}{4}$
(B_2M)[c]	3	$\frac{3}{2}$	1	$\frac{3}{4}$	$\frac{3}{8}$
$(BM)_2$	4	2	$\frac{4}{3}$	1	$\frac{1}{2}$
$(BM)_4$	8	4	$\frac{8}{3}$	2	1

[a] B = $\overset{(-)}{\mathrm{OR}}$ and M = $\overset{(+)}{\mathrm{K}}$ or $\overset{(+)}{\mathrm{Na}}$. [b] M is counterion. [c] (BM_2) is counterion.

In the reaction with t-C_4H_9OK–THF, ion-pair tetramer[13] is the dominant species and the apparent kinetic order in base 0·40 thus agrees best with the theoretical value 0·375 expected for ion triplet $(\overset{-}{(RO)_2}\overset{+}{M})$ as the active base. In the reaction with t-C_4H_9OK–t-C_4H_9OH as well as with t-C_4H_9ONa–t-C_4H_9OH, ion-pair monomer is the dominant species[15] and the experimental values of *d*/*a* approaching unity (1·14 and 0·83, respectively) suggest that the dominant species serves also as the active base.

Analogous assessments of active base species have been accomplished previously also in other reactions with t-C_4H_9OK–THF and t-C_4H_9OK–t-C_4H_9OH. In *syn*- and *anti*-dehydrochlorination from 3,4-dichloro-2,2,5,5-tetramethylhexane with t-C_4H_9OK–THF Schlosser and An[18] determined kinetic orders in base 0·5 and 0·8 respectively, and suggested that ion-pair dimer is the active base in the former (*syn*) and ion pair trimer or tetramer in the latter (*anti*) reaction. The same conclusion has been drawn[18] also from the apparent orders in base 0·5 – 0·7 and 0·9 – 1·2 determined in the corresponding reactions with t-C_4H_9OK–t-C_4H_9OH, on the incorrect[15] assumption that ion pair tetramer is the dominant base. Pritchard[19] observed 3/2 kinetic order in base in t-C_4H_9OK–t-C_4H_9OH promoted proton abstraction from 1-halo-2,2-diphenylethylenes and proposed that ion triplet is the active base. Cram with coworkers[20] found a greater than a second-order dependence on base in t-C_4H_9OK–t-C_4H_9OH promoted D/H exchange from 2-octylsulphone and suggested that ion pair aggregate is the active base.

Justifiability of such simple assessments of active base becomes however questionable when the individual reactions are further probed. As Table II shows, olefin-isomer distribution (orientation) in the reaction of 2-decyl bromide with all the three base–solvent systems we now have under study varies markedly with the analytical concentration of the alkoxide base. Percentage of 1-alkene always increases whereas that of *trans*-2-alkene decreases as the concentration of base is being enhanced. Accordingly kinetic orders in base for the individual olefin-forming processes in the reaction are different being significantly higher for the 1-alkene than for the *trans*-2-alkene (Table V).

TABLE V

Kinetic order in base determined for the individual olefin-isomer forming pathways

Base/Solvent	Kinetic order in base[a]		
	1-decene	*cis*-2-decene	*trans*-2-decene
tert-C_4H_9OK/THF[b]	0·44 ± 0·02	0·49 ± 0·03	0·33 ± 0·02
tert-C_4H_9OK/tert-C_4H_9OH	1·17 ± 0·06	1·10 ± 0·04	1·02 ± 0·04
tert-C_4H_9ONa/tert-C_4H_9OH	0·86 ± 0·04	0·80 ± 0·03	0·69 ± 0·06

[a] Mean values and standard mean deviations. [b] Tetrahydrofuran.

In a recent study we showed[3] that such orientational changes as observed in Table II are by no means exceptional but rather a normal feature in alkali alkoxide promoted elimination from alkyl halides and tosylates, at least in low polar solvents. Similar changes were noted also in the elimination from some cycloalkyl derivatives[4,5] even in a dipolar solvent[5].

Two hypotheses have been proposed for the effect of base concentration, one assuming a competition of two or more active base species[2] and the other a substrate solvation by metal alkoxide[3]. Kinetic analysis of the two hypotheses follows.

Parallel Reactions of Two or More Active Base Species with a Single Substrate

Let us consider a general model of base species competition in which n active base species A_i participate in the reaction with a substrate S so that each species A_i contributes to the overall reaction velocity by

$$v_i = k_i[A_i]\,[S]\,. \tag{7}$$

For the overall velocity then holds

$$v = \sum_i v_i = \sum_i k_i[A_i]\,[S]\,. \tag{8}$$

If all equilibria

$$d_i\,D \overset{K_i}{\rightleftarrows} a_i A_i \tag{9}$$

are very fast (relative to v_i), for each $[A_i]$ holds

$$[A_i] = K_i^{1/a_i}\,[D]^{d_i/a_i}\,. \tag{10}$$

When $\sum_i [A] \ll [D]$, it is possible to rewrite the Eq. (*10*) as

$$[A_i] \approx K_i^{1/a_i}\,[ROM_t]^{d_i/a_i} \tag{11}$$

and substituting for $[A_i]$ in the Eq. (*8*) we obtain

$$v \approx \sum_i k_i K^{1/a_i}\,[ROM_t]^{d_i/a_i}\,[S]\,. \tag{12}$$

Replacing $k_1 K^{1/a_1}$ by k_i^* we obtain

$$v = \sum_i k_i^*\,[ROM_t]^{d_i/a_i}\,[S] \tag{13}$$

which is a general polynomial function with respect to the concentration $[ROM_t]$.

From the mathematical point of view it is possible to solve the Eq. (*13*) with respect to the n unknowns k_i if, and only if

$$d_i/a_i \neq d_j/a_j \quad \text{for} \quad i \neq j \tag{14}$$

for all pairs of indices *i* and *j*. If for some pair of *i* and *j* holds

$$d_i/a_i = d_j/a_j \tag{15}$$

then contributions from the corresponding active base species A_i and A_j are indistinguishable and this pair must be treated in its entirety.

Using the experimental data from Tables I and II (*cf.* Eq. (*3*)), the Eq. (*13*) has been solved for all possible combinations of the active base species listed in Table IV. The results of this calculation are presented in Tables VI – VIII.

As these results show, the experimental data from the reaction of 2-decyl bromide with all the base–solvent systems studied are compatible with the model of base species competition based on the Eq. (*13*). Three different combinations of active base species are "allowed" in the reaction with t-C_4H_9OK–THF (Table VI), eight combinations are "allowed" with t-C_4H_9OK–t-C_4H_9OH (Table VII) and four are "allowed" with t-C_4H_9ONa–t-C_4H_9OH (Table VIII).

TABLE VI

Calculated contributions (%) of competing base species in olefin formation from 2-decyl bromide with t-C_4H_9OK–THF

[Base][a]	Base species combination[b]			*(II + III)*			*II*			*cis-III*			*trans-III*		
	A_1	A_2	A_3	A_1	A_2	A_3	A_1	A_2	A_3	A_1	A_2	A_3	A_1	A_2	A_3
1·00	(B)	$(BM)_4$		50	50	—	45	55	—	37	63	—	62	38	—
0·50				65	35	—	60	40	—	53	47	—	75	25	—
0·25				77	23	—	73	27	—	67	33	—	85	15	—
0·10				88	12	—	86	14	—	82	18	—	93	7	—
1·00	(BM)	$(BM)_4$	—	67	33	—	60	40	—	50	50	—	83	17	—
0·50				77	23	—	72	28	—	63	37	—	89	11	—
0·25				85	15	—	81	19	—	73	26	—	93	7	—
0·10				92	8	—	89	11	—	85	15	—	96	4	—
1·00	(B)	(B_2M)	$(BM)_4$	12	68	19	7	69	24	20	31	48	19	79	2
0·50				15	71	13	9	74	17	28	35	36	21	77	1
0·25				19	72	9	12	77	11	36	38	25	25	74	1
0·10				23	72	5	15	79	6	46	39	15	29	70	1

[a] Titrimetrical concentration of t-C_4H_9OK. [b] Other combinations of the active base species listed in Table IV do not give a physically meaningfull solutions (contributions > 0) for all olefin--isomers.

TABLE VII

Calculated contributions (%) of the competing base species in olefin formation from 2-decyl bromide with t-C_4H_9OK in tert-butanol

[Base][a]	Base species combination[b]			(*II* + *III*)			*II*			*cis-III*			*trans-III*		
	A_1	A_2	A_3	A_1	A_2	A_3	A_1	A_2	A_3	A_1	A_2	A_3	A_1	A_2	A_3
0·67	(B)	(B_2M)	—	14	86	—	11	89	—	19	81	—	29	71	—
0·33				25	75	—	20	80	—	32	68	—	45	55	—
0·16				41	59	—	35	65	—	50	50	—	63	37	—
0·07				61	39	—	55	45	—	69	31	—	80	20	—
0·67	(BM)	(B_2M)	—	39	61	—	30	70	—	55	45	—	85	15	—
0·33				48	52	—	38	62	—	62	37	—	89	11	—
0·16				57	43	—	47	53	—	71	29	—	92	8	—
0·07				66	34	—	57	43	—	79	21	—	95	5	—
0·67	(B)	$(BM)_2$	—	27	73	—	25	75	—	32	68	—	40	60	—
0·33				52	48	—	49	51	—	57	43	—	66	34	—
0·16				76	24	—	74	26	—	80	20	—	85	15	—
0·07				92	8	—	91	9	—	93	7	—	95	5	—
0·67	(BM)	$(BM)_2$	—	60	40	—	55	45	—	71	29	—	90	10	—
0·33				74	24	—	71	29	—	83	17	—	95	5	—
0·16				86	14	—	84	16	—	91	9	—	97	3	—
0·07				94	6	—	92	8	—	96	4	—	99	1	—
0·67	(B)	(BM)	$(BM)_2$	14	30	56	15	22	63	11	46	42	13	62	25
0·33				23	39	35	29	29	42	19	55	25	19	67	13
0·16				40	41	19	46	32	22	29	58	13	27	66	6
0·07				55	38	7	62	29	9	41	54	5	38	60	2
0·67	(B)	$(BM)_4$	—	42	58	—	40	60	—	46	54	—	52	48	—
0·33				90	10	—	89	11	—	91	9	—	93	7	—
0·16				99	1	—	99	1	—	99	1	—	99·4	0	—
0·07				100	0	—	100	0	—	100	0	—	100	0	—
0·67	(BM)	$(BM)_4$	—	74	26	—	70	30	—	80	20	—	92	8	—
0·33				96	4	—	95	5	—	97	3	—	99	1	—
0·16				100	0	—	100	0	—	100	0	—	100	0	—
0·07				100	0	—	100	0	—	100	0	—	100	0	—
0·67	(B)	(BM)	$(BM)_4$	2	71	27	1	68	30	2	77	21	8	79	13
0·33				3	93	4	2	93	5	3	94	3	12	86	2
0·16				4	95	1	3	96	0	5	95	0	17	83	0
0·07				7	93	0	5	95	0	7	93	0	23	77	0

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[a] Titrimetrical concentration of t-C_4H_9OK. [b] Other combinations of active base species listed in Table IV do not give physically meaningfull solutions (contributions > 0) for all olefin isomers.

TABLE VIII

Calculated contributions (%) of the competing base species in olefin formation from 2-decyl bromide with t-C_4H_9ONa in tert-butanol

[Base][a]	Base species combination[b]		(*II* + *III*)		*II*		*cis-III*		*trans-III*	
	A_1	A_2	A_1	A_2	A_1	A_2	A_1	A_2	A_1	A_2
0·51	(B)	(BM)	34	66	28	72	37	63	69	31
0·26			42	58	35	65	45	55	76	24
0·14			50	50	42	58	53	47	81	19
0·05			62	38	55	45	65	35	88	12
0·51	(B)	(B_2M)	58	42	53	47	59	41	82	18
0·26			73	27	69	31	74	26	90	10
0·14			83	17	81	19	84	16	94	6
0·05			93	7	92	8	94	6	98	2
0·51	(B)	$(BM)_2$	66	34	62	38	67	33	86	14
0·26			84	16	82	18	85	15	95	5
0·14			93	7	92	8	93	7	98	2
0·05			98	2	98	2	98	2	99	1
0·51	(B)	$(BM)_4$	75	25	72	28	76	24	92	8
0·26			97	3	96	4	97	3	99	1
0·14			100	0	100	0	100	0	100	0
0·05			100	0	100	0	100	0	100	0

[a] Titrimetrical concentration of t-C_4H_9ONa. [b] Other combinations of active base species listed in Table IV do not give physically meaningfull solutions (contributions > 0).

Next the data in Tables VI–VIII show that the contributions from the individual base species are concentration-dependent. The contribution from the least associated species (A_1) always decreases while that from the most associated one (A_3 or A_2) increases as the total concentration of base is being enhanced. As a simple consideration of the Eq. (*13*) may show, such a dependency will arise whenever the competing species differ in the state of association, as a consequence of different partial orders in base (d_i/a_1).

At last, inspection of Tables VI–VIII shows that selectivities of the competing base species are different. In any "allowed" combination, the least associated species A_1 contributes always more to the formation of *trans*-2- than *cis*-2- and 1-alkene. The exact opposite holds for the most associated species A_3 (or A_2). This difference becomes more clearly apparent from Table IX summarizing regioselectivities (1-alkene/*trans*-2-alkene ratios) and stereoselectivities (*trans*-2-alkene/*cis*-2-alkene ratios) of the individual competing species calculated from the data in Tables II and VI–VIII. Noteworthy are, in particular, the values for the most associated species A_3 (or A_2): As Table IX shows, the calculated 1-alkene/*trans*-2-alkene ratios for this species are in most instances very high (10–30) whereas the ratios *trans*-2-alkene/*cis*-2-alkene are extremely low (0·1–1·0).

It follows that this model calculation is in a perfect accord both with the hypothesis assuming a concentration-dependent competition[2,4] of several base species differing in selectivity as well as with the hypothesis assuming *cis*-stereoselectivity of associated alkoxide base[6–8] in the reaction (*anti*-elimination[1]).

TABLE IX

Calculated regioselectivities (*II*/*trans-III* ratios) and stereoselectivities (*trans-III*/*cis-III* ratios) of the individual base species competing in the elimination from 2-decyl bromide

Base species combination			(*II*/*trans-III*)[a]			(*trans-III*/*cis-III*)[a]		
A_1	A_2	A_3	A_1	A_2	A_3	A_1	A_2	A_3
t-C_4H_9OK–tetrahydrofuran[b]								
(B)	$(BM)_4$	—	1·2	2·5	—	5·3	1·9	—
(BM)	$(BM)_4$	—	1·2	3·8	—	5·2	1·1	—
(B)	(B_2M)	$(BM)_4$	0·6	1·5	22	2·9	8·2	0·1
t-C_4H_9OH–tert-butanol[c]								
(B)	(B_2M)	—	2·9	9·9	—	1·6	0·9	—
(BM)	(B_2M)	—	2·8	38	—	1·6	0·3	—
(B)	$(BM)_2$	—	4·7	9·3	—	1·3	0·9	—
(BM)	$(BM)_2$	—	4·6	35	—	1·3	0·3	—
(B)	(BM)	$(BM)_2$	8·9	2·6	23	1·2	1·4	0·6
(B)	$(BM)_4$	—	5·5	9·3	—	1·2	0·9	—
(BM)	$(BM)_4$	—	5·5	30	—	1·2	0·4	—
(B)	(BM)	$(BM)_4$	1·1	6·4	16	4·2	1·1	0·7
t-C_4H_9ONa–tert-butanol[d]								
(B)	(BM)	—	2·5	14	—	2·0	0·5	—
(B)	(B_2M)	—	3·9	16	—	1·5	0·5	—
(B)	$(BM)_2$	—	4·3	18	—	1·4	0·4	—
(B)	$(BM)_4$	—	4·6	21	—	1·3	0·1	—

[a] Average from the values obtained for different concentrations of the total base indicated in Table II. Standard deviation from the average value was in most instances smaller than 10%. [b] Calculated from data in Tables II and VI. [c] From data in Tables II and VII. [d] From data in Tables II and VIII.

Parallel Reactions of the Free (Uncomplexed) and the Alkoxide-Complexed Substrate with a Single Active Base

Let us next consider a simple model of substrate solvation by metal alkoxide in which a free substrate S_f is in a rapid equilibrium with the complex $S\cdots D$ arising by coordination of the substrate leaving group (electron donor) with one molecule of metal alkoxide in the dominant form D (electron acceptor):

$$S_f + D \overset{K_c}{\rightleftharpoons} S\cdots D\,. \tag{C}$$

If the free and the complexed substrates react simultaneously with an active base A so that the former contributes to the overall reaction by

$$v_f = k_f[S_f]\,[A] \tag{16}$$

and the latter by

$$v_c = k_c[S\cdots D]\,[A] \tag{17}$$

then for the overall reaction velocity holds

$$v = k_f[S_f]\,[A] + k_c[S\cdots D]\,[A]\,. \tag{18}$$

If

$$[S_f] + [S\cdots D] = [S_t] \tag{19}$$

and

$$K_c = \frac{[S\cdots D]}{[S_f]\,[D]} \tag{20}$$

and

$$[D] \sim [\mathrm{ROM_t}]\,, \tag{21}$$

where $[S_t]$ and $[\mathrm{ROM_t}]$ are total concentrations of substrate and the alkoxide base, respectively, the Eq. (*18*) can be rewritten as

$$v = k_f\frac{[S_t]\,[A]}{1 + K_c[\mathrm{ROM_t}]} + k_c\frac{K_c[S_t]\,[A]\,[\mathrm{ROM_t}]}{1 + K_c[\mathrm{ROM_t}]} \tag{22}$$

and substituting for A from the Eq. (5) we obtain

$$v = k_f\frac{K^{1/a}[S_t]\,[\mathrm{ROM_t}]^{d/a}}{1 + K_c[\mathrm{ROM_t}]} + k_c\frac{K_cK^{1/a}[S_t]\,[\mathrm{ROM_t}]^{(1+d/a)}}{1 + K_c[\mathrm{ROM}]_t}\,. \tag{23}$$

Since K_c for solvation of alkyl halides by metal alkoxides in electron-donating solvents such as tetrahydrofuran and tert-butanol is expected to the smaller than unity and since also $[\mathrm{ROM_t}]$ in Table I is invariably smaller than unity, it can be assumed that under conditions of the present study holds

$$K_c[\mathrm{ROM_t}] \ll 1 \tag{24}$$

so that the Eq. (*23*) reduces to

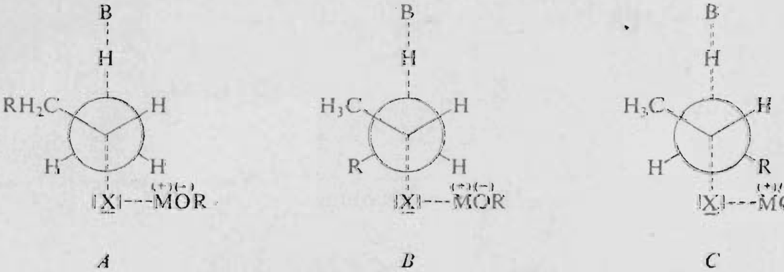
$$v = k_f K^{1/a}[\mathrm{S_t}]\,[\mathrm{ROM_t}]^{d/a} + k_c K_c K^{1/a}[\mathrm{S_t}]\,[\mathrm{ROM_t}]^{(1+d/a)} \tag{25}$$

which is a special case of the polynomial function (*12*).

Using the experimental data from Tables I and II, the Eq. (*25*) has been solved for all active base species listed in Table IV. Physically meaningfull solutions (contributions >0) were obtained in all the three base–solvent systems studied; however only when dissociated or monomeric ion-paired species served as the active base. The results are summarized in Tables X and XI.

Table X shows that the calculated contributions of the free and the complexed substrate are concentration-dependent, the former decreasing and the latter increasing as the total concentration of base is being enhanced. Table XI shows that calculated selectivities in the elimination from the free and the complexed substrate are different, the former contributing always more to *trans-III* while the latter more to *cis-III* and *II*-alkene formation.

This pattern of results agrees well with the recent suggestion[3] that the effect of base concentration on orientation, such as shown in Table II, arises from an external* solvation of leaving group in substrate by metal alkoxide. According to this suggestion (Scheme 2), steric interference between the metal alkoxide and the alkyl portion of the substrate creates hindrance to the solvation in the transition state for *trans-III* alkene formation (*C*). In the transition state for the terminal alkene *II* and *cis-III*



SCHEME 2

alkene (A and B, respectively), the solvation is unaffected because the solvating molecule has a free access from that side where only hydrogens are placed. Since the solvation is assumed to lower energy of transition state considerably, k_c in the Eq. (*25*) is expected to be substantially larger than k_f. Steric hindrance to the solvation may therefore affect orientation even if K_c is small.

TABLE X

Calculated contributions (%, under assumption that $K_c[ROM_t] \ll 1$) of the uncomplexed and the alkoxide-complexed forms of 2-decyl bromide (S_f and S_c, respectively) in the reaction with different base–solvent combinations

[Base][a]	Active[b] species	*(II + III)*		*II*		*cis-III*		*trans-III*	
		S_f	S_c	S_f	S_c	S_f	S_c	S_f	S_c
		t-C_4H_9OK–tetrahydrofuran							
1·00	(B)	52	48	48	52	40	60	64	36
0·50		69	31	65	35	57	43	78	22
0·25		81	19	78	22	72	28	88	12
0·10		92	8	90	10	87	13	95	5
1·00	(BM)	71	29	65	35	55	45	86	14
0·50		83	17	79	21	71	28	92	8
0·25		91	9	88	12	83	17	96	4
0·10		96	4	95	5	92	8	98	2
		t-C_4H_9OK–tert-butanol							
0·67	(B)	14	86	11	89	19	81	29	71
0·33		25	75	20	80	32	68	45	55
0·16		41	59	35	65	50	50	63	37
0·17		61	39	55	45	69	31	80	20
0·67	(BM)	60	40	55	45	71	29	90	10
0·33		76	24	71	29	82	17	95	5
0·16		86	14	84	16	91	9	97	3
0·07		94	6	92	8	96	4	99	1
		t-C_4H_9ONa–tert-butanol							
0·51	(B)	58	42	53	47	59	41	82	18
0·26		73	27	69	31	74	26	90	10
0·14		83	17	81	19	84	16	94	6
0·05		93	7	92	8	94	6	98	2

[a] Titrimetrical concentration of metal alkoxide. [b] Other active species than those indicated do not give physically meaningfull solutions (*i.e.* contributions > 0) of the Eq. (*25*) for all olefin-isomers.

TABLE XI

Calculated regioselectivities (*II*/*trans-III* ratios) and stereoselectivities (*trans-III*/*cis-III* ratios) in the reaction of the free and alkoxide-complexed 2-decyl bromide (S_f and S_c, respectively), with a single active base

Base/Solvent	Active species	(*II*/*trans-III*)[a]		(*trans-III*/*cis-III*)[a]	
		S_f	S_c	S_f	S_c
t-C_4H_9OK/THF	(B)	1·2	2·5	5·1	1·8
	(BM)	1·3	3·9	4·9	1·0
t-C_4H_9OK/t-C_4H_9OH	(B)	2·9	9·9	1·6	0·9
	(BM)	4·6	35	1·4	0·3
t-C_4H_9ONa/t-C_4H_9OH	(B)	3·9	16	1·5	0·5

[a] Calculated from data in Tables II and X. Average from the values obtained for the different concentrations of the total base indicated in Table II. Deviations from the average value were invariantly smaller than 10%.

Summing up we can conclude that the experimental data from Tables I and II are perfectly compatible both with concept assuming a competition of several active base species as well as with that assuming a competition between free and alkoxide-complexed substrate in the reaction. In this way it follows that assessment of active base in the reaction is model-dependent.

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* In contrast to the internal solvation of the leaving group by the approaching active base[6,8] which is implicit in the concept of base species competition.

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Translated by the author (J. Z.).