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CONSTITUTIONAL EFFECTS ON THE COMPETING SYN- AND ANTI-PATHWAYS IN BIMOLECULAR ELIMINATION: COMMENTS ON THE BROWN-INGOLD CONTROVERSY[1,2]

M. Pánková and J. Závada*

Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, Prague, Czechoslovakia

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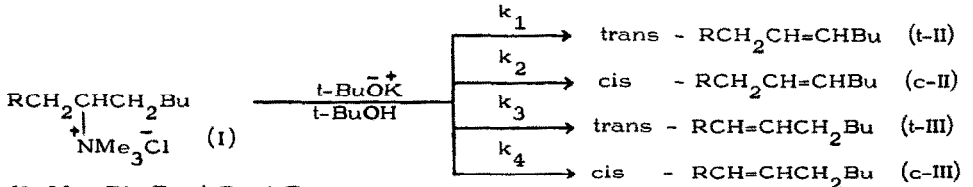
The question whether steric[3] or polar[4] effects control the course of E2 reactions in open-chain systems was discussed ardently during past decades and opposing views (Brown-Ingold controversy) remained irreconciled[5]. Our discovery that E2 reactions do not always proceed homogeneously by the anti-mechanism, as it was originally anticipated, but may represent a blend of two mechanistic (syn- and anti-) pathways[6] placed the "old" problem into a new light: in particular, it showed that the constitutional effect in both the competing pathways has to be examined, at least in those processes where the dual elimination mode is pronounced.

This, obviously, poses a task of a very considerable complexity which can be approached unambiguously only by combination of kinetic data from appropriate reaction series and "static" data for the proportions[6,7] of the participating mechanisms to the individual olefin-isomer formation. Earlier approaches based only on the kinetic[4], or on the "static"[7] data are bound to be uncertain, and lead, eventually, to incorrect conclusions.

We now wish to report an approximate analysis of the complex problem for the E2 reaction of the alkyltrimethylammonium chlorides I with potassium t-butoxide in t-butanol. Standard kinetic procedures employing an efficient v.p.c. technique[8] allowed a quantitative determination of the overall (syn + anti) rate constants for the individual olefin-isomer formation (k_1, k_2, k_3 and k_4). Next, the overall rate constants for the trans-alkenes formation, k_1 and k_3, were dissected into the syn- and anti-components ($k_{s\rightarrow t\text{-II}}$, $k_{a\rightarrow t\text{-II}}$ and $k_{s\rightarrow t\text{-III}}$, $k_{a\rightarrow t\text{-III}}$, respectively). For some derivatives it could be per-



R = H, Me, Et, Pr, i-Pr, t-Bu

formed quantitatively, on basis of the reported[6a] contributions of the two alternative pathways to the particular isomer formation. For other derivatives, where the data were not available, values from closely related systems[6a,7] had to be used in the calculation.

In the cis-alkene formation, the contributions of the syn-pathway are known to be generally small (<10%) and could therefore be omitted in the calculation, the overall rate constants k_2 and k_4 being put equal to $k_{a\rightarrow c\text{-II}}$ and $k_{a\rightarrow c\text{-III}}$, respectively. The results are given in Table 1.

TABLE 1 Approximate Rate Constants for Main Elimination Pathways in E2 Reaction of the Quaternary Salts I with t-BuOK in t-BuOH at 35°C

R	$10^7 k$ ($sec^{-1}mol^{-1}$ l) [a]					
	s→t-II	a→t-II	a→c-II	s→t-III	a→t-III	a→c-III
H	1.2	6.9	32.4		(4010) [b]	
Me	66.2	13.6	27.2	97.3	42.7	198.0
Et	74.6	9.2	24.8	76.0	15.6	28.8
n-Pr	85.8	10.7	35.[illegible]	85.8	10.7	35.6
i-Pr	141.0	9.0	[illegible]4.1	27.0	≤3.0	1.5
t-Bu	428.0	4.3	7.6	9.4	≤1.0	0.05

[a] Calculated from the equations (1) and (2): $k^s = k^{tot} \times (\%syn/100)$; $k^a = k^{tot} \times (\%anti/100)$. The syn- and anti-contributions (%syn and %anti) from related alkyl($\overset{+}{N}Me_3$) ⟶ (trans-)alkene transformations (in t-BuOK-t-BuOH or t-PeOK-t-PeOH) were used in the calculation as follows : 2-hexyl⟶2-hexene for II: R=H, 3-hexyl⟶2-hexene for III: R=Me, 3-hexyl⟶3-hexene for II: R=Me and III: R=Et, 5-decyl⟶5-decene for II: R=Et and III: R=Pr. For II and III: R=i-Pr we used average of the values reported for II: R=Pr and t-Bu and III: R=Pr and t-Bu, respectively. Direct experimental values were used for II: R=Pr and for II and III: R=t-Bu. For compilation of the data see ref. 6a.

[b] Overall (syn- + anti-) rate constant for 1-heptene formation.

Examine first the processes proceeding in direction "away" from the variable R group. Here, by general consent[3,4], the polar influence of R is only of a minor, if any importance: steric effects in both the syn- and anti-pathways can therefore be appreciated immediately from the rate trends.

A gradual, and very pronounced increase of rates with increasing steric bulk of R is found for the s⟶t-II elimination. Contrary to previous expectations[9], it reveals that steric strain must be present in ground states of the onium salts examined and be relieved[10], substantially, on going to the transition states[8]: the C-$\overset{+}{N}$ bond loosening is presumed to provide the driving force.

By contrast, no relief of strain is observed in the alternative anti-pathways (a⟶t-II and a⟶c-II). The rates remain practically constant within the series and decrease, in actual fact, slightly for the most strained derivative (R=t-Bu). This, obviously, might come as a surprise, for, particularly in the trans-alkene formation, alleviation of strain of the molecular framework should ensue from C-$\overset{+}{N}$ bond loosening in the syn- as well as in the anti-pathway[11]. However, steric hindrance to base approach[3,7] has also to be taken into account in the anti-pathway. The group R was proposed[7] to shield hydrogens in the anti-position and to enforce an efficient rate control, down to the simplest alkyl structures. While the present data disprove, in actual fact, the claim concerning the rate control, the hindrance[12] nonetheless may be involved in the re-

action. Considering circumstances, one is tempted to suggest that balance rather than absence of steric factors accounts for apparent lack of steric control in the a→t-II and a→c-II pathways.

Examine next the eliminations in direction "towards" the substituent R. The C-H bond to be broken is now exposed fully to the influence of R; consequently, steric as well as polar effects have to be considered in analysis of the observed rate trends (s→t-III, a→t-III, a→c-III).

It has been proposed by Ingold[4] that distinction between steric and polar effects can be made in kinetic series on following grounds: "Owing to the steep bank in the non-bonding energy curve, a steric effect, once it starts, should build up very rapidly with increasing material density about reaction site. On the other hand, an electrostatic effect is subject to the attenuation of relay, and thus should show gentler and more monotonous forms of variation, which can be predicted by empirical comparisons and also roughly computed".

By qualitative inspection as well as by the comparisons proposed[4], it is the polar form of variation which is displayed in both the syn- and anti-pathway. This[13], notably, was found also by Ingold in the related elimination series[14] $RCH_2.CHR'.\overset{+}{N}Me_3$ (R' = H and t-Bu, respectively) and interpreted as being evidence that steric effects are absent[15] in the reaction.

However, arguments may be given against drawing any simple conclusions from these findings. We already pointed out previously[8b] that steric effects in elimination do not always follow the predicted (telescope) form of rate variation but may exhibit the polar pattern[16]. Significantly, this holds also for the present series: a very monotonous rate trend[17] is observed in the s→t-II pathway although the substituent effect involved is beyond reasonable doubts of steric origin.

Therefore, while polar effects admittedly play a very important role in the reaction, steric effects should not be dismissed from considerations on such grounds. The factors operating in the alkene-II formation may be involved more generally in E2 reactions and participate in the rate control. In the present case, it may explain well the different magnitude of the substituent effect in the alternative pathways for the alkene-III formation, for, whereas relief of steric strain is presumed[10] to attenuate the inductive effect on rate in the syn-pathway, steric hindrance may tend to reinforce it in the anti-pathways.

REFERENCES AND NOTES

1. This is the thirtieth of a series of papers dealing with mechanism of elimination reactions; for previous paper see ref. 2.
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8. (a) J. Závada, J. Sicher: Collection Czechoslov. Chem. Commun. 32, 3701 (1967), (b) J. Závada, M. Pánková, M. Svoboda: ibid, in the press.
9. Increase of steric strain is predicted by the steric theory for transition state of E2 reactions (ref. 3). In the polar theory, on the other hand, steric strain is predicted to be negligible in the ground as well as transition state (ref. 4). However, for correct prediction see J. Bunnett: Angew. Chem. 74, 731 (1962).
10. Analogous effect is found both for t-II and III in the Cope elimination of the corresponding amine oxides (ref. 8b).
11. For evidence that relief of strain is not a privilege of syn-elimination but may occur also in the anti-pathway see J. McKenna, J.M. McKenna, R. Ledger, P.B. Smith: Tetrahedron 20, 2423 (1964).
12. Hindrance to base approach was also proposed to explain the preferential cis-alkene formation in the anti-pathway. However, there are different opinions concerning the origin of the hindrance (ref. 2 and 7).
13. A very satisfactory linear correlation is obtained by plotting log k for alkene-III formation against the corresponding data from the Ingolds' series.
14. Exclusive anti-elimination was assumed in the two series. The present evidence (ref. 6a, 7) suggests that syn-elimination contributes non-negligibly in the former (R'=H), and considerably in the latter (R'=t-Bu) series.
15. Except for the most branched group (R=t-Bu) in β position (neohexyl anomaly; ref. 4).
16. It has been pointed out previously (J. Hendrickson: J. Am. Chem. Soc. 83, 4537 (1961)) that much of accommodation of a molecule to strain can be accomplished by adjustment of bond angles. This may account for the "polar" form of steric effects, for, in contrast to steep bank of energy curve for non-bonding interactions, the bond angle strain is known to be subject to a more monotonous form of variation.
17. Noteworthy, a very satisfactory fit is also obtained by plotting log $k_{s \rightarrow t\text{-II}}$ against the Taft polar substituent constants, σ^*. For analogous observations concerning the Cope elimination see ref. 8b.