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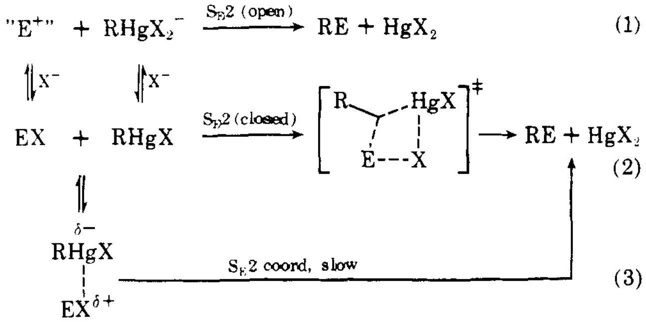
A Rate Sequence for S_E2 Retention with Large Steric and Large Electronic Effects

Sir:

Relative rate sequences are useful for explaining reactivity trends with respect to mechanism and for the assignment of mechanisms to new reactions. For S_N2 reactions the principal effect of structure on rate is one of steric retardation upon increased branching at the α- and β-carbon atoms, understood in terms of a "pentavalent" inversion transition state.[1] For S_N1 (carbonium ion) reactions electronic effects are paramount.[2] In contrast to nucleophilic substitution, there are no simple rules for electrophilic aliphatic substitution governing either stereochemistry or the interplay of steric and electronic substituent effects.[3] Presented herein for an S_E2 reaction which proceeds with retention of configuration is a rate sequence which indicates the superposition of a large steric effect on an opposing large electronic effect.

Electrophilic cleavages of alkylmercuric halides exhibit marked catalysis by added halide ion, which can be rationalized in terms of improved leaving group ability and enhanced C–Hg bond nucleophilicity, provided by either (i) a pre-kinetic equilibrium complexing of the substrate organomercurial, forming $RHgBr_2^-$ (eq 1), or (ii) a pre-kinetic equilibrium complexing of the electrophile "E^+", which effects reaction via the concerted S_E2 (closed) (eq 2) or the two-step S_E2 (coordination) (eq 3) mechanism.[3,4]



The present study examined the reaction of a series of (saturated) alkylmercuric bromides with bromine in methanol

$$\mathrm{RHgBr + Br_2 \xrightarrow[\text{methanol}]{\mathrm{Br^-}\ \text{(large excess)}} RBr + HgBr_2} \qquad (4)$$

wherein the effects of branching in the α-, β-, and γ-carbon atoms could be independently assessed. The catalytic effect of added bromide ion was studied by measuring rates as a function of [Br^-] at a constant ionic strength of 0.30 M (NaBr plus $NaClO_4$). The progress of reaction was followed spectrophotometrically (monitoring the disappearance of bromine color[5]) at 25.0 °C, and first-order dependence in each reactant was demonstrated. The rates of the uncatalyzed reactions are very slow and could not be measured with reproducible accuracy;[6] so only the rates of the one-anion-catalyzed reactions

$$\mathrm{Br_2 + RHgBr_2^-} \xrightarrow{k_{3A}}$$

$$\mathrm{Br_3^- + RHgBr} \xrightarrow{k_{3B}} \qquad (5)$$

are reported here. Pseudo-third-order rate constants (Table I), referring to either of two kinetically indistinguishable reactions (eq 5), were obtained from the experimentally observed second-order rate constants according to the following analysis:

Table I. Pseudo-Third-Order Rate Constants for the One-Bromide Ion-Catalyzed Bromine Cleavage of Alkylmercuric Bromides in Methanol at 25.0 °C at 0.30 M Ionic Strength

	RHgBr, R	$k_{3A}K_2$ or $k_{3B}K_1$, $s^{-1}\,M^{-2}$
α branching	methyl	1.68
	ethyl	18.1
	isopropyl	1310
	tert-butyl	5660
β branching) (primary R)	ethyl	18.1
	n-propyl	7.43
	isobutyl	2.09
	neopentyl	0.2903
β branching (secondary R)	isopropyl	1310
	sec-butyl	1016
	$Me_2CHCH(Me)$-	
	$Me_3CCH(Me)$-	53.3
γ branching) (primary R)	*n*-propyl	7.43
	n-butyl	8.32
	$Me_2CHCH_2CH_2$-	
	$Me_3CCH_2CH_2$-	12.5

$$\text{rate} = k_{\text{obsd}}[\mathrm{Br_2}]_t[\mathrm{RHgBr}]_t \qquad (6)$$

(subscript t refers to the summed concentration of all forms of the reactant)

$$\mathrm{Br_2 + Br^-} \overset{K_1}{\rightleftharpoons} \mathrm{Br_3^-} \quad \mathrm{RHgBr + Br^-} \overset{K_2}{\rightleftharpoons} \mathrm{RHgBr_2^-} \qquad (7)$$

$$\text{rate} = k_2[\mathrm{Br_2}][\mathrm{RHgBr}] + \begin{Bmatrix} k_{3A}[\mathrm{Br_2}][\mathrm{RHgBr_2^-}] \\ \text{or} \\ k_{3B}[\mathrm{Br_3^-}][\mathrm{RHgBr_2}] \end{Bmatrix} \qquad (8)$$

$$k_{\text{obsd}} = \frac{k_2 + \begin{Bmatrix} k_{3A}K_2 \\ \text{or} \\ k_{3B}K_1 \end{Bmatrix} [\mathrm{Br^-}]}{\{1 + K_1[\mathrm{Br^-}]\}\{1 + K_2[\mathrm{Br^-}]\}} \qquad (9)$$

The value of K_1 (methanol, 25 °C, μ = 0.2 M) has been determined[8] to be 177 M^{-1}. Although no systematic measurement of the mercurial equilibrium constants K_2 has been performed, the handful of published data indicates that these

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values are on the order of 1 M^{-1} and, surprisingly, are more or less independent of structure of the R group.[9] Thus, at low $[Br^-]$, $(1 + K_2[Br^-])$ approaches unity, and eq 9 can be rewritten to show that a plot of $k_{obsd}(1 + K_1[Br^-])$ vs. $[Br^-]$ should yield a straight line with slope of $k_{3A}K_2 = k_{3B}K_1$. The values obtained in this way are listed in Table I.

Methyl for hydrogen substitution at the α carbon results in a large rate acceleration: apparently the electron-donating alkyl inductive effect helps assuage an electron deficiency which develops at the reaction center during electrophilic cleavage by the highly electronegative halogen.[10] For β branching, the electronic substituent effect is attenuated[11] and should thus result in a smaller rate increase; however, a large rate *decrease* is observed, in line with a steric effect (most probably due to van der Waals repulsion in the bimolecular transition state).

The present reaction occurs with retention of configuration[12] and, hence, might have been expected to exhibit an α-branching steric effect, consistent with other front-side cleavages.[13,14] In order to reconcile the experimental data in terms of a single mechanism, it is concluded that an α-steric effect does operate but is masked by an opposing very large electronic effect. For the case of β branching, the now reduced electronic effect is overshadowed by a continued large steric effect (perhaps more severe than for α branching), which is unusual for a retention reaction.[15] Branching at the γ carbon results in a small rate increase, again in the direction of a dominating electronic effect (which should be much attenuated at this position, so that any steric effect must now be very small).

It should be noted that the data do not permit a differentiation between the two kinetic terms possible for one-anion catalysis (eq 5).

Only limited and usually incomplete structure-activity data are available for S_E2 reactions. For those that have been shown to occur with *retention* of configuration at carbon, an examination of the effect on rate of α branching has yielded predominantly polar sequences[16] and predominantly steric sequences,[13] as well as "mixed" sequences.[17] The results presented herein suggest that the interplay of steric and electronic effects may not be revealed unless an examination of the effect of branching is extended to include the β and γ positions as well.

For those S_E2 reactions that have been shown to occur with *inversion* of configuration at carbon, only steric rate sequences (which exhibit different structural dependencies) have so far been observed.[18,19] However, with the proper selection of system, it may be possible to observe polar (and "mixed") sequences here as well, thus completing the structure-activity spectrum for both S_E2 stereochemical classes.

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Photochemical Formation of *trans*-1-Phenylcyclohexene. Chemical Proof of Structure†

Sir:

In a flash photolysis study of *cis*-1-phenylcyclohexene, a transient has been observed to which the structure of *trans*-1-phenylcyclohexene has been assigned.[1] This structural assignment to the transient was based upon the chemistry that it displayed and upon the insensitivity of its lifetime to the polar nature of the solvent. The short lifetime of this new species in methanol at room temperature, $\tau = 9$ μs, was attributed to a fast thermal trans-cis isomerization. This process is apparently slowed down by lowering of the reaction temperature; using data between +30 and −40 °C, the plot of $\log(1/\tau) = f(1/T)$ gave a straight line, indicating an activation energy of ~7.5 kcal/mol. When the temperature was lowered below −50 °C, the lifetime increased less than that predicted from the Arrhenius plot. Thus, the lifetime in methanol at −70 °C of the postulated trans species is only 500 μs, a value nearly ten times smaller than calculated.[2] This observed shorter lifetime could be due to the involvement of a second deactivation process of the postulated trans species which has a low activation energy and which becomes competitive at this lower temperature.

The product(s) formed via this new process was investigated and we present here new chemical evidence which clearly indicates the formation of *trans*-1-phenylcyclohexene by direct irradiation of its cis isomer.

Upon irradiation of *cis*-1-phenylcyclohexene in neutral methanol (0.02 M) at room temperature, the major process is the [2 + 2] dimer formation (58%);[3] the generation of a methyl ether is of minor importance (3%).[4] When the irradiation is conducted in acidic methanol, the yield of methyl

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† This paper is dedicated to Professor E. Havinga on the occasion of his retirement from the Chair of Organic Chemistry at the University of Leiden.

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