in the triplet energy transfers between acetone and olefins. Now, an assignment of about 1 kcal/mole lower triplet energy (E_T) per alkyl substituent in ethylene appears reasonable,[10,11] since observations a and b indicate that an energy difference of 0.7 kcal/mole for E_T's in C_2H_4 and C_2D_4 introduces an energy transfer rate ratio of about 1.8.

Several conclusions follow: (1) observations a and b indicate that the acceptor excitation process in the triplet energy transfer and the O_2-induced S → T absorption process are alike with regard to the observed deuterium isotope effects; (2) observations a and c strongly suggest that the rate-determining factors in the appropriate combinations of radiationless transitions during the collisional encounter of the donor and the acceptor are largely *intramolecular* in nature,[12] and they suggest further that the lifetime variation of the donor-acceptor collision pair is not likely to be important in governing the variations of the relative quenching efficiencies (for a given donor); (3) observation d implies that the chief rate-controlling factor for the energetically unfavorable collisional energy-transfer processes is the extent of the overlap between the de-excitation function of the donor and the excitation function of the acceptor (radiative as well as radiationless transition probability *vs.* energy); and (4) the reason for the lack of large deuterium rate isotope and alkyl substitution effects in quenching the Hg($^3P_1$) atom by olefins[13] lies in the fact that this triplet energy transfer process is favorably exothermic and that the deuterium isotope effect is more pronounced at the transition thresholds.[14,15]

We believe that the measurement of the deuterium rate isotope effect is useful as a probe in the study of the intermolecular electronic energy-transfer processes, as has been demonstrated in the study of the Franck–Condon factors and the *intramolecular* relaxation processes.[16,17] Further study on the donor isotope effect will be useful in establishing the mechanism in greater detail.

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(10) Each alkyl substituent in ethylene raises the efficiency of quenching of the triplet donors by a factor of 2 (see ref 1 and 2).

(11) Analogous rate–energy correlations for a variety of the donor–acceptor pairs have been observed in the condensed phase studies: (a) G. Porter and F. Wilkinson, *Proc. Roy. Soc.* (London), **A164**, 1 (1961); (b) K. Sandros and H. L. J. Backstrom, *Acta Chem. Scand.*, **16**, 958 (1962); (c) W. G. Herkstroeder and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).

(12) See for example the discussion of the isotope effect observed in the phosphorescence lifetimes of acetone-d_6 and acetone-h_6 in the frozen medium by R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966); acetone-d_6 has a much longer intramolecular relaxation time than acetone-h_6.

(13) (a) H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, 1, 209 (1963); (b) R. J. Cvetanović, *Progr. Reaction Kinetics*, **2**, 39 (1964).

(14) A. A. Gordus and R. B. Bernstein, *J. Chem. Phys.*, **22**, 790 (1954).

(15) It is observed that k_H/k_D for the pair 1,3-butadiene and 1,3-butadiene-d_6 in quenching the triplet C_6H_6 is 1.0 ± 0.2 while k_H/k_D in quenching the triplet biacetyl ($E_T = 57$ kcal/mole) is 2.0 ± 0.3. The details of this study will soon be published.

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(17) W. Siebrand and D. F. Williams, *J. Chem. Phys.*, **46**, 403 (1967).

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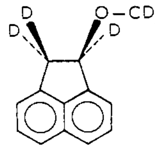
Effect of Cation on the Stereochemistry of Hydrogen–Deuterium Exchange

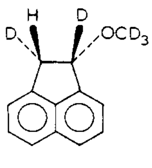
Sir:

We have observed an inversion in the stereochemistry of base-catalyzed hydrogen–deuterium exchange dependent only on the nature of the cations present in solution. The rigid system, 1-trideuteriomethoxy-1,2,2-trideuterioacenaphthene (I), was prepared and the deuterons were exchanged in *t*-butyl alcohol. The base varied from lithium *t*-butoxide through the potassium to tetramethylammonium salts.

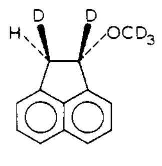


I

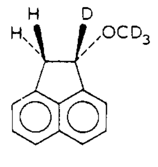
Experimentally the substrate (0.04–0.16 *M*) was treated in sealed, degassed tubes under the conditions reported in Table I. Concurrent with an elimination reaction producing acenaphthylene, exclusive exchange at the 2 positions was observed. Thus the products of exchange are *cis*-h_1, *trans*-h_1, and h_2 as designated below.



trans-h_1



cis-h_1



h_2

The olefin–ether mixture was analyzed by vpc and the mixture separated by elution chromatography. The exchanged ether was distilled (>80% recovery) and analyzed by nmr (15 wt % in CCl_4) for relative amounts of protons *cis* and *trans* to the OCD_3 group.[1] Isotopic analysis by mass spectrometry (Varian M-66) determined the relative amounts of d_6, d_5, and d_4 material. Combination of both pieces of information allows an estimate of the amounts of I, *cis*-h_1, *trans*-h_1, h_2, and acenaphthylene as reported in Table I.

The results of run 1 of Table I with tetramethylammonium *t*-butoxide as base show preferential hydrogen incorporation *trans* to the methoxyl group (*i.e.*, more *trans*-h_1 than *cis*-h_1). Runs 2 and 3 with potassium *t*-butoxide show just the opposite behavior with hydrogen incorporation occurring predominantly *cis* to the methoxyl group. With lithium *t*-butoxide, runs 4 and 5, exchange occurred exclusively *cis* to the methoxyl group. These changes are demonstrated more clearly by converting the data of Table I into the k^{cis}/k^{trans} ratios reported in Table II.

The rate ratio has changed by at least a factor of 45 depending on the nature of the cation with the exchange preference crossing from predominantly *trans* to exclusively *cis*. Although the calculated ratio, k^{cis}/k^{trans}, will depend upon the elimination reaction, preliminary results indicate that the actual ratio for lithium would

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(1) Stereochemical assignments are based upon coupling constants obtained from an ABX analysis of the spectrum of 1-trideuteriomethoxyacenaphthene (δ_{cis} 3.11 ppm, δ_{trans} 3.32 ppm, δ_X 5.06 ppm, $J_{cis,trans}$ = 17.2 Hz, $J_{cis,X}$ = 2.7 Hz, $J_{trans,X}$ = 6.9 Hz) and upon the agreement of these coupling constants and relative chemical shifts with about 20 1-substituted acenaphthenes (S. Sternhell, private communication).

Table I. Products of Exchange and Elimination of Ether I with *t*-Butyl Alcohol–*t*-Butoxide

	Base				Ethers				%
Run	Cation[a]	Concn, *M*	Temp, °C[b]	Time, min	% I	% *cis*-h_1	% *trans*-h_1	% h_2	acenaphthylene
1	$(CH_3)_4N^+$	0.11	45	500	50	12	30	<1	8
2	K^+	0.43	85	188	38	23	11	7	21
3	K^+	0.43	85	500	9	18	5	14	54
4	Li^+	0.14	160	1010	51	17	0.4	1	31
5	Li^+	0.14	160	4023	8	18	<0.4	2	72

[a] Present as the *t*-butoxide salt. [b] ±0.05°.

Table II. The Effect of Cation on the Relative Rates of Exchange *cis* and *trans* to the β-Methoxyl Group

Cation	k^{cis}/k^{trans} [a]
$(CH_3)_4N^+$	0.36
K^+	2.2
Li^+	>16

[a] k^{cis}/k^{trans} = ln (1 − fraction *cis* protons)/ln (1 − fraction *trans* protons).

be higher. It is interesting to note that the preference for exchange *cis* to the methoxyl group increased as the coordinating ability of the cation increased. On this basis the role of the cation can be visualized in terms of the intermediate (II) in the partial reaction scheme for *cis* exchange (Figure 1).

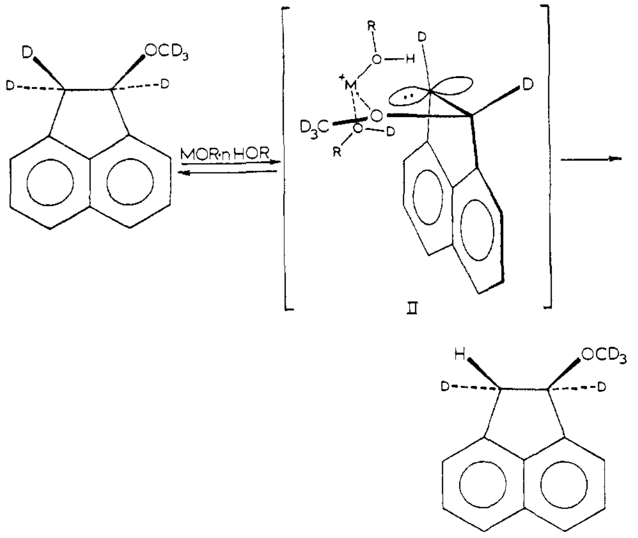

Figure 1.

With lithium as cation (M^+) exchange could then occur entirely through this intermediate producing only *cis* exchange. As with potassium *t*-butoxide in *t*-butyl alcohol,[2] under these conditions the base probably exists as a solvated ion pair or agglomerate as indicated by the more stringent conditions required for reaction. Approach of the ion pair to the side of the molecule on which the methoxyl group is situated would be favored by the high solvation energy of lithium cations. This coordinated ion pair could then remove the *cis* deuteron. Rotation of the coordinated cation and its solvent sheath with subsequent proton donation would lead to stereoselective *cis* exchange.

With tetramethylammonium *t*-butoxide, the active base is suspected to be dissociated *t*-butoxide anions[3] and the above reaction scheme would not apply. Instead the preferential formation of *trans*-h_1 could reflect the steric effect of a β-methoxyl group on deuteron abstraction by *t*-butoxide anion and proton donation by *t*-butyl alcohol. With potassium *t*-butoxide in *t*-butyl alcohol, the moderate preference for *cis* exchange might result from either an intermediate (II) less tightly bound than with lithium or alternatively a competition between free *t*-butoxide anions and ion pairs as the active bases.

The preferential exchange at the 2 positions rather than the 1 position seems to be attributable to carbanion destabilization by an electronegative group as has been discussed by both Cram[4] and Hine.[5]

Coordination to alkali metal cations has often been implicated in intermediates formed during base-catalyzed hydrogen–deuterium exchange of carbon acids.[6] However, the effect on stereospecificity of changing the alkali metal cation of alkoxide bases has normally been small,[2a,7] with quaternary ammonium cations providing the greatest variation in behavior.[8] Coordination of divalent oxygen or trivalent nitrogen with sodium or potassium ions has been invoked to rationalize the dominating formation of *cis* isomers in the base-catalyzed allylic isomerizations of allylic ethers and amines.[9] But dependence on cation has not been established.

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