triplet acetone with **3**, i.e., not so much slower than the rate of quenching of triplet acetone by oxygen.

(19) The emitter has not yet been identified in this case in the absence of fluorescer or in the case of **2**.

(20) Induced decomposition is the likely cause of the erroneously high rate ($t_{1/2}$ = 102 min at 56°, two orders of magnitude faster than observed here) reported by Mazur and Foote,[5] since their experiment was done with pure **1** by NMR.

(21) P. S. Engel and B. M. Monroe, *Adv. Photochem.*, **8**, 245 (1971).

(22) At 20°, ϕ_F^{DBA} = 0.1 (ref. 21). The activation energy of the fluorescence of DBA is ~−4.5 kcal.

(23) By a static method similar to that of Berenfel'd et al., ref 24; T. Wilson, unpublished results.

(24) V. M. Berenfel'd, E. V. Chumaevskii, M. P. Grinev, Yu. I. Kuryatnikov, E. T. Artem'ev, and R. V. Dzhagatspanyan, *Bull. Acad. Sci. USSR, Phys. Ser. (Engl. Transl.)*, **3**, 597 (1970).

(25) V. A. Belyakov and R. F. Vassil'ev, *Photochem. Photobiol.*, **11**, 179 (1970).

(26) This calls for a correction in the calculation of $^3\phi$, to take into account the fraction of ^{1}DBA* which can be expected to receive its excitation from singlet carbonate by s–s transfer. This correction is based on the value of y intercept with DPA multiplied by ϕ_F^{DBA} (~0.04, at the temperature of this experiment).

(27) H. C. Steinmetzer, P. Lechtken, and N. J. Turro, *Justus Liebigs Ann. Chem.*, 1984 (1973).

(28) The somewhat shorter lifetimes derived from the diene experiments can probably be attributed to quenching of the carbonyls by the dioxetanes themselves, present at higher concentrations in the diene experiments, as well as to quenching by DBA. Quenching of DPA and DBA fluorescences by the dienes is negligible under the present conditions.

(29) In the case of **3**, the present value of $\tau' k_{ss}$ = 67 M^{-1} (Table II, column 4) is about five times smaller than reported by Steinmetzer et al.[27] Here, if τ = 2 × 10^{-9} s^{-1} (for singlet excited acetone), then $k_{ss} \simeq 3 \times 10^{10}$ M^{-1} s^{-1}.

(30) (a) H. K. Eigenmann, D. M. Golden, and S. W. Benson, *J. Phys. Chem.*, **77**, 1687 (1973); (b) S. W. Benson and R. Shaw in "Organic Peroxides", D. Swern, Ed., Vol. 1, Wiley-Interscience, New York, N.Y., p 105. (c) This method has proven its usefulness in the case of tetramethyldioxetane (ΔH_{calcd} = −68.8 kcal, ΔH_{obsd} = −71 ± 3 kcal); see P. Lechtken and G. Höhne, *Angew. Chem. Int. Ed. Engl.*, **12**, 772 (1973), and H. E. O'Neal and W. H. Richardson, *J. Am. Chem. Soc.*, **92**, 6553 (1970), and correction, *ibid.*, **93**, 1828 (1971).

(31) Note, however, that the energies of one of the groups entering the calculation is unknown and had to be assigned (see footnote c, Table IV). Nevertheless, this reaction can be expected to have a large exothermicity in view of the stabilization energy of methyl carbonate (~25 kcal).

(32) L. W. Johnson, H. J. Maria, and S. P. McGlynn, *J. Chem. Phys.*, **54**, 3823 (1971).

(33) The validity of this assumption of exothermic transfer has been discussed for **3** (ref 1c) and for **4** (ref 13).

(34) A factor of ~2, because of the steepness of the slope of this 1/[DPA] plot.

(35) Most other methods for determining yields of excited products suffer from similar difficulties; see ref 2. In any case, the yields of excited products obtained here from **3** are not significantly different from the literature values.[1c,10b]

(36) W. H. Richardson, M. B. Yelvington, and H. E. O'Neal, *J. Am. Chem. Soc.*, **94**, 1619 (1972).

(37) These authors have also viewed their reported agreement between the observed values of kinetic parameters for several small dioxetanes and those calculated on the basis of a diradical mechanism, as another argument in favor of nonconcertedness. The difficulty here lies in the assumptions entering the calculations. For example, for **1**, Richardson et al. estimate that at 56° k_1 = 8 × 10^{-5} s^{-1}, which is two orders of magnitude higher than the observed rate.

(38) (a) M. J. S. Dewar and S. Kirschner, *J. Am. Chem. Soc.*, **96**, 7578, 7579 (1974); (b) N. J. Turro and A. Devaquet, *ibid.*, **97**, 3859 (1975).

The Measurement and Interpretation of Hydrogen–Tritium Kinetic Isotope Effects in Borane and Borohydride Reductions of Ketones. Implications on Steric Approach Control vs. Product Development Control[1]

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Abstract: Hydrogen–tritium isotope effects have been measured for the reduction of a series of ketones with borane and sodium borohydride. The isotope effects for the reductions are contrasted with those in the hydroboration of alkenes and are discussed in terms of the thermodynamics and kinetics of the reactions. It is concluded that both the reduction and hydroboration reactions involve four-center transition states leading to product formation; however, the extent of bonding between the various atoms in the four-center transition states differs significantly. These differences are discussed in terms of the relative strengths of the bonds being formed and broken in the transition states. The implications of the isotope effects on steric approach control and product development control are discussed.

Introduction

The concepts of steric approach control (SAC) and product development control (PDC), initially introduced by Dauben in 1956,[2] have been subjected to considerable scrutiny, particularly in their application to the reduction of substituted cyclohexanones to which the concepts were originally applied. The presence of SAC has been accepted in these and many other reactions; the presence of PDC, however, has proved more elusive to demonstrate, and considerable effort has been expended to either support or refute its operation. Although a number of slightly different definitions have been advanced to replace the original definitions of SAC and PDC,[3-5] the basic difference between SAC and PDC centers on the position of the transition state along the reaction coordinate,[5] i.e., whether the steric interactions in the transition state are of the long-range type between the

attacking reagent and the substrate molecule, which is in its ground-state geometry (an early transition state), or steric interactions present in the product (a late transition state). Several authors have suggested that the sodium borohydride reduction of ketones proceeds via an early transition state (no PDC),[5-9] Eliel and Senda have suggested "PDC plays at best a minor role",[4] while others have suggested that late transition states are involved[10-13] (PDC operative).

One of the techniques used to gain information concerning the extent of bond formation (or cleavage), i.e., the position of the transition state along the reaction coordinate, makes use of the measurement and interpretation of kinetic isotope effects (KIE). Even here, however, controversy reigns. Geneste and Lamaty[13a] have measured the secondary H–D KIE in the sodium borohydride reduction of α-deuterated ketones and interpreted the data in terms of

a late transition state. Laszlo and Welvart, however, have interpreted these results in terms of an early transition state.[14] Wigfield and Phelps[5,9] have measured the primary H–D KIE in the reduction of cyclohexanones with sodium borohydride and sodium borodeuteride deriving inverse KIE's (i.e., $k_H/k_D < 1$). These inverse KIE's were interpreted as arising from a normal primary KIE (i.e., $k_H/k_D > 1$) which is overwhelmed by a triple inverse secondary KIE.[5,9] Wigfield and Phelps' KIE's do not display any immediately apparent trend with the position or degree of substitution on the cyclohexanone system. In order to avoid the complicating secondary H–D KIE's, Wigfield and coworkers[15] carried out reductions with lithium tributoxyaluminohydride (and deuteride). With most ketones, H–D KIE's range 1.0–1.5, but the reduction of the highly hindered ketones, 3,3,5,5-tetramethyl- and 4-acetyl-3,3,5,5-tetramethylcyclohexanone, are associated with inverse isotope effects of 0.79 and 0.70, respectively.

In an extension of our studies on the hydroboration of alkenes,[16] including the measurement of hydrogen-tritium KIE's,[16a] we have measured the H–T isotope effects for the borane and sodium borohydride reduction of ketones. The interpretation of the KIE data thus derived is not complicated by interfering secondary KIE's owing to the extremely low atom percent of tritium present, and allows for a comparison of trends in the KIE's with those observed in hydroboration; a reaction proceeding via a well-defined early transition state.
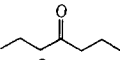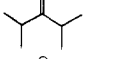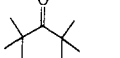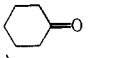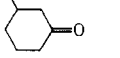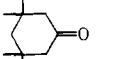
Results

Borane Reduction of Ketones. Preliminary to the reductions of the ketones with tritium labeled borane, the reactivities of the substrates toward reduction with unlabeled borane (0.4–0.5:1.0 mol ratio substrate:borane) in tetrahydrofuran were measured by GLC techniques, and the nature of the reduction products was determined by ^{11}B NMR. As the degree of substitution at the α carbon increases, the rate of reduction markedly decreases; for example, 3-heptanone undergoes very rapid reduction (complete within a minute) while 2,2,4,4-tetramethyl-3-pentanone (di-*tert*-butyl ketone) requires approximately 24 h for complete reduction. In all cases the *only* product formed was the dialkoxyborane; in no case could a monoalkoxyborane be observed as an intermediate.[17] In a much slower reaction

$$R_2CO + BH_3 \xrightarrow[\text{slow}]{} R_2CHOBH_2 \xrightarrow[\text{fast}]{R_2CO} (R_2CHO)_2BH$$

the dialkoxyboranes undergo redistribution to an equilibrium mixture of di- and trialkoxyborane and borane.[18] These data indicate that the initially formed monoalkoxyborane is considerably more reactive toward reduction than is borane.[19] Further complicating the picture is the possibility of H–T exchange between products and unreacted borane, which would continuously increase the tritium content of the borane as the reaction proceeds. The values of the H–T KIE's appearing in Table I have been calculated[21] on the basis of no B–H,B–T exchange, and rapid exchange, these values representing extremes for the KIE's in the presence of exchange. It should be noted that the values for no exchange and with exchange differ by less than 10%, and that no change in relative trends occurs. Should exchange be occurring, the true value of the KIE will fall between the no exchange and exchange values.

Sodium Borohydride Reduction of Ketones. The kinetics of the reactions of sodium borohydride with ketones have been studied by Wigfield and Phelps,[5] and Brown and coworkers,[22] the reactions being first order in both ketone and borohydride. The rate-determining step is proposed to in-

Table I. H–T KIE's for the Reduction of Carbonyl Compounds with Borane in Tetrahydrofuran at 25°

Carbonyl compd	No B–H exchange	With B–H exchange
(1)	6.69	6.22
(2)	8.70, 8.29[a]	8.04, 7.62[a]
(3)	11.1	10.3
(4)	8.90, 8.46[a]	8.20, 7.74[a]
(5)	9.23	8.48
(6)	8.28	7.71

[a] Duplicate determination.

volve hydride transfer from borohydride to form an alkoxyborohydride; however, the alkoxyborohydride and subsequently formed di- and trialkoxyborohydrides are also reducing agents[22] capable of reducing the ketones. Unfortunately, we have not been able to identify the nature of the reduction products by ^{11}B NMR. Incremental addition of a ketone to a solution of sodium borohydride in 2-propanol resulted in a diminution of the borohydride quintet; however, no other peaks corresponding to the possible alkoxyborohydrides were observed. Apparently, moderately rapid exchange of the ligands attached to boron of the alkoxyborohydrides is occurring (on the NMR scale), which results in extreme line broadening and destruction of the $^1H \rightarrow {}^{11}B$ coupling, but exchange with borohydride is slow.

Table II lists the calculated KIE's for formation of various alkoxyborohydrides as products in the absence and presence of H–T exchange. As the molar ratio of ketone:borohydride employed in these experiments was one, values for the KIE's for $ROBH_3^-$ formation in the absence of exchange cannot be calculated, while the KIE's for $(RO)_4B^-$ formation in the absence of exchange will be unity. It should be noted that there is again little difference in the values of the KIE's as calculated by the various approaches, and no changes in the relative trends are noted.

Discussion

In the ensuing discussion we wish to compare the reduction of ketones with borane and sodium borohydride with the hydroboration of alkenes. The hydroboration of an alkene occurs via an early transition state.[16a] Essentially no rehybridization of the carbon atoms of the double bond has occurred in going to the transition state as evidenced by the lack of torsional angle effects.[23,24] The facial selectivity of attack by borane on the double bond is controlled by long-range steric interactions between the incoming borane and functions attached to remote portions of the alkene (for example, the axial 3 and 5 positions in substituted cyclohexenes).[23] The H–T KIE's observed in the hydroboration reaction decrease markedly as the degree of substitution on the double bond increases (see Table III). This trend has been interpreted in terms of less C–H bond formation and less B–H bond cleavage in the transition state as the steric hindrance to addition to the double bond increases.[16] Also included in Table III are relative reactivities of various alkenes toward hydroboration. It is important to note that the KIE's vary substantially, but that the relative rates range

Table II. H–T KIE's for Reduction of Ketones with Sodium Borohydride in 2-Propanol

Ketone	Product					
	ROBH$_3^-$ (exchange)	(RO)$_2$BH$_2^-$ (no exchange)	(RO)$_2$BH$_2^-$ (exchange)	(RO)$_3$BH$^-$ (no exchange)	(RO)$_3$BH$^-$ (exchange)	(RO)$_4$B$^-$ (exchange)
1	3.65	4.22	3.46	3.80	3.40	3.37
2	5.04	5.62	4.82	5.21	4.75	4.72
3	5.25	5.80	5.03	5.41	4.97	4.92
4	4.03	4.68	3.81	4.21	3.75	3.72
5	3.81	4.41	3.60	3.97	3.54	3.51
6	3.38	3.90	3.21	3.52	3.16	3.13

Table III. Relative Reactivities and H–T KIE's for the Hydroboration of Alkenes

	Rel reactivity[a]	H–T KIE[b]
Monosubstituted alkenes		
1-Hexene	100	9.59
Styrene	19	9.09, 9.00[c]
Disubstituted alkenes		
3-Hexene		6.92
2-Octene		7.38
2-Ethyl-1-hexene		7.47
2-Pentene	37	(7.4)[d]
2-Methyl-1-pentene	102	(7.4)[d]
Trisubstituted alkene		
2-Methyl-2-butene	23	3.63
Tetrasubstituted alkene		
2,3-Dimethyl-2-butene	7	2.91

[a] With BH$_3$ in diglyme (see ref 26). [b] From ref 16a. [c] Terminal and internal addition KIE's. [d] Projected as the average from 2-octene and 2-ethyl-1-hexene.

Table IV. Enthalpy of Reaction and Activation for Sodium Borohydride Reduction of Acetone and Hydroboration of 2,3-Dimethyl-2-butene

	$\Delta H°$, kcal mol^{-1}	$\Delta H‡$, kcal mol^{-1}
Hydroboration of 2,3-dimethyl-2-butene	−99[a]	9.0[b]
Sodium borohydride reduction of acetone	−128.2[c]	8.8[d]
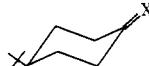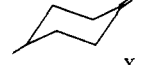
[a] Estimated for the reaction BH$_3$ + H$_2$C=CH$_2$ → B(C$_2$H$_5$)$_3$ from data for the reactions 2BH$_3$ ⇌ B$_2$H$_6$ (ref 27) and B$_2$H$_6$ + 6H$_2$C=CH$_2$ → 2B(C$_2$H$_5$)$_3$ (ref 28). See also ref 16. [b] From ref 16. [c] From ref 29. [d] From ref 30.

only over a factor ∼14. There is no apparent correlation between H–T KIE and relative reactivity.

Thermodynamically, the reduction of ketones with sodium borohydride is virtually identical with the hydroboration of alkenes. The activation enthalpies are within experimental error (see Table IV), while on a per B–H bond consumed basis, the $\Delta H°$'s also agree within experimental error. Although similar data for the borane reduction of ketones are not available, the consideration of bond energies in model systems indicates that the $\Delta H°$ per B–H bond consumed should be similar to those for hydroboration and borohydride reduction. Stereochemically, however, the sodium borohydride reduction of substituted cyclohexanones and the hydroboration of substituted methylenecyclohexanes differ.[31] The reduction reaction is sterically more sensitive to substituents at the 2-axial and 2-equatorial positions than is hydroboration, and thus the total steric effects exerted by all portions of the molecule are different in the two reactions[32] (see Table V). The facial selectivities of the borane and sodium borohydride reductions, on the other hand, are very similar.

Analysis of the KIE and relative reactivity data for the reduction of ketones with sodium borohydride (Table VI)

Table V. Stereoselectivities in Ketone Reductions and Hydroboration

Substrate	Reducing agent (X = O) (% cis product)		Hydroboration (X = CH$_2$) (% cis product)
	BH$_3$	NaBH$_4$[g]	BH$_3$
	8 (0°)–16 (100°)[a]	14.6[b]	68[c]
			33[c]
	12[d]	25[e]	63[c]
			34[c]
	26[f]	31[e]	
	34[d]	36–37[b]	

[a] Reference 33. [b] Reference 4. [c] Reference 31. [d] Reference 20. [e] Reference 5. [f] Reference 34. [g] In 2-propanol.

Table VI. H–T KIE's and Relative Reactivities in the Sodium Borohydride Reduction of Ketones

Ketone[d]	H–T KIE[a]	$k \times 10^4$, 1. mol^{-1} sec^{-1}
1	3.46	2.10[b]
2	4.82	0.549[b]
3	5.03	0.016[b]
4	3.81	765[c]
5	3.60	605[c]
6	3.21	1.92[c]

[a] KIE's for (RO)$_2$BH$_2^-$ formation with exchange. [b] Reference 30. [c] Reference 5. [d] Structures in Table I.

reveals trends considerably different from those apparent in the hydroboration of alkenes (Table III). Most significantly, the KIE's in the ketone reductions vary little over a reactivity range of ∼45 000! In addition, in the acyclic ketone series, which can be considered as acyclic analogues of 2-axial and 2-equatorial substituted cyclohexanones, the KIE's *increase* slightly with *decreasing* reactivity (and increasing steric inhibition to attack at the carbonyl carbon). In contrast, in the 3- (and 5-) substituted cyclohexanones, the KIE's *decrease* slightly with *decreasing* reactivity. (In the substituted cyclohexanones we have not differentiated between the KIE's for axial and for equatorial attack or on different conformations by hydride; the indicated KIE's represent a weighted average for the two modes of reaction.) The differences in the trends of the KIE's with position of substitution parallel the relative importance of steric effects of 3-axial vs. 2-axial and 2-equatorial substituents in

Table VII. Experimental Data for Reduction of Carbonyl Compounds with Borane in Tetrahydrofuran at 25°

Ketone	Moles of ketone, ($\times 10^3$)	Alcohol, cpm/mol ($\times 10^9$)	Moles of $BH_3{}^a$ ($\times 10^2$)
1	7.58	1.247	1.725
2	8.00	1.270	1.725
	7.94	1.260	1.605
3	6.91	1.141	1.725
4	10.89	1.220	2.30
	11.12	1.180	2.14
5	11.27	1.288	2.30
6	11.27	1.434	2.30

a 4.574×10^9 cpm/mol.

Table VIII. Experimental Data for the Reduction of Ketones with Sodium Borohydride in 2-Propanol at 25°

Ketone	Mol of ketone reacted/ mol of $NaBH_4{}^a$	Cpm/mol of alcohol ($\times 10^8$)
1	1.000	10.23
2	0.780	9.33
3	0.729	9.53
4	1.000	9.39
5	1.000	9.82
6	1.000	1.099

a 0.121 M $NaBH_4$ in 2-propanol, 3.372 $\times 10^9$ cpm/mol.

cyclohexanones.[31,32] The KIE's for the reduction of the ketones with borane exactly parallel those of the borohydride reductions. This is in keeping with the similarities in facial selectivities of attack and relative reactivities.

In order to relate the obvious similarities of the reaction thermodynamics, but dissimilar facial selectivities of reaction and KIE's with reactivity in the ketone reduction and hydroboration reactions in terms of related mechanisms, we must consider in greater detail the strengths of the bonds being formed and broken in the two processes. In the hydroboration reaction, the strongest bonds involved in the reaction are the C-H (95-99 kcal per mol) and B-H ($\geq$80 kcal per mol) bonds (the strength of the π component of the double bond is $\sim$63 kcal per mol, while the strength of the B-C bond is $\leq$80 kcal per mol). In the ketone reductions, the strongest bond involved is the B-O bond ($\sim$110 kcal per mol), while the π component of the C=O is $\sim$90 kcal per mol and the C-O and C-H bond strengths are $\sim$83 and 95-99 kcal per mol. Both the hydroboration[16] and borane reduction[35] reactions are proposed to proceed via borane substrate complexes which rearrange to product. The similarities between the borane and borohydride reductions are suggestive that the borohydride reduction also occurs in a similar manner. Provided that the rearrangement of the complex is rate determining, KIE's of greater than unity are expected for early rearrangement transition states;[36] i.e., the small inverse equilibrium isotope effect for complex formation is overwhelmed by the normal isotope effect in the rate-determining rearrangement step. In the thermodynamics of the hydroboration process, the cleavage of the B-H and formation of the C-H bonds dominate (i.e., are the strongest bonds being formed or broken) resulting in KIE's, the magnitude of which is expected to vary with the degree of H transfer. In the thermodynamics of the ketone reduction processes, the cleavage of the π component of the C=O and formation of the B-O bond dominate. In this case, the strongest bonds being formed or broken do not involve the H (or T) resulting in H-T KIE's, the magnitude of which might not be expected to be sensitive to steric effects and overall reactivity. The rearrangement transition states therefore resemble a "four-directional, cyclic teeter-totter" in which the bonds of highest energy (i.e., the "heaviest bonds") dominate the balance of the energetics of the bonding processes.

Should the formation of the complex become rate determining, such as might be expected in the cases of very sterically bulky, unreactive borohydrides and carbonyl compound substrates, an inverse isotope effect might be expected by extrapolation of the trend in the H-T KIE's for the substituted cyclohexanones illustrated in Tables I, II, and VI.[38]

The initial impetus for the measurement of the H-T

KIE's for ketone reduction reactions was the hope that the data might shed some light concerning the position of the transition state along the reaction coordinate, i.e., whether SAC or PDC is operative. Unfortunately, we do not feel that the present data uniquely allow for such a distinction. Comparison of the KIE's and steric effects suggests that the transition state for hydride transfer in a probable complex occurs considerably later along the reaction coordinate in the reduction reactions than in the hydroboration reaction. It is obvious that more information is required to more clearly define the role and effects of complex formation.

Experimental Section

Measurement of the KIE's for Reduction of Ketones with Borane in Tetrahydrofuran. A stock solution of tritium-labeled borane in tetrahydrofuran was prepared as described previously.[16] The concentration of borane was determined by hydrolysis and measurement of the amount of hydrogen evolved. The tritium content was determined by reaction of the labeled borane with an excess of 1-hexene followed by oxidation and hydrolysis and isolation of the hexanol by preparative GLC techniques and measuring the tritium content of the hexanol by standard counting procedures. The carbonyl compounds were subjected to reduction with borane at 25° for periods of time sufficient to ensure complete reduction (determined by control reactions monitored by GLC) except with diisopropyl and di-tert-butyl ketone for which the extent of reduction was determined in each case by GLC at the end of 24-36 h. The alcohols were isolated by hydrolysis and extraction and were purified by distillation, sublimation, or preparative GLC. Table VII lists the moles of reactants and activities of the borane and product alcohols.

Measurement of the KIE's for Reduction of Ketones with Sodium Borohydride in 2-Propanol. A standard stock solution of tritium-labeled sodium borohydride in 2-propanol was prepared. The tritium content was determined by reaction of an aliquot of the solution with an excess of hexanal followed by isolation and counting of the 1-hexanol as described above. The various ketones were reacted with the sodium borohydride and the alcohols isolated and purified as outlined above. The extent of reduction in each case was determined by GLC or by NMR techniques. Table VIII lists the ratios of moles of ketone reacted per mole of sodium borohydride and the activities of sodium borohydride and the product alcohols.

References and Notes

(1) Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research (Grant No. 1225, A1-3) and to the National Institutes of Health for partial support (Grant No. CA-07194).
(2) W. G. Dauben, G. J. Fonken, and D. S. Noyce, J. Am. Chem. Soc., 78, 2579 (1956).
(3) H. C. Brown and H. R. Deck, J. Am. Chem. Soc., 87, 5620 (1965).
(4) E. L. Eliel and Y. Senda, Tetrahedron, 26, 2411 (1970).
(5) D. C. Wigfield and D. J. Phelps, Can. J. Chem., 50, 388 (1972).
(6) J. C. Richer, J. Org. Chem., 30, 324 (1965).
(7) M. Cherest, H. Felkin, and N. Prudent, Tetrahedron Lett., 2199 (1968); M. Cherest and H. Felkin, ibid., 2205 (1968).
(8) D. C. Ayres, D. N. Kirk, and R. Sawdaye, J. Chem. Soc. B, 505 (1970).

(9) D. C. Wigfield and D. J. Phelps, *Chem. Commun.*, 1152 (1970).
(10) H. C. Brown and K. Ichikawa, *Tetrahedron*, 1, 221 (1957).
(11) H. Kwart and T. Takeshita, *J. Am. Chem. Soc.*, **84**, 2833 (1962); K. Bowden and M. Hardy, *Tetrahedron*, **22**, 1169 (1966).
(12) P. T. Lansbury and R. E. MacLeay, *J. Am. Chem. Soc.*, **87**, 831 (1965); G. J. Karabatsos and T. H. Althuis, *Tetrahedron Lett.*, 4911 (1967).
(13) (a) P. Geneste and G. Lamaty, *Bull. Soc. Chim. Fr.*, 699 (1968); *Tetrahedron Lett.*, 4633 (1965); (b) P. Geneste, G. Lamaty, and J. P. Roque, *ibid.*, 5007 (1970).
(14) P. Laszlo and Z. Welvart, *Bull. Soc. Chim. Fr.*, 2412 (1966).
(15) D. C. Wigfield, D. J. Phelps, R. S. Pottie, and R. Sander, *J. Am. Chem. Soc.*, **97**, 897 (1975).
(16) (a) D. J. Pasto, B. Lepeska, and T. C. Cheng, *J. Am. Chem. Soc.*, **94**, 6083 (1972); (b) D. J. Pasto, B. Lepeska, and V. Balasubramaniyan, *ibid.*, **94**, 6090 (1972).
(17) A similar observation has been reported for the reactions of alcohols with borane.[18]
(18) D. J. Pasto, V. Balasubramaniyan, and P. W. Wojtkowski, *Inorg. Chem.*, **8**, 594 (1969).
(19) The kinetics of the reduction of ketones with borane in tetrahydrofuran have been investigated.[20] It is claimed that the reaction is first order in ketone and three-halves order in "diborane". Unfortunately, no product studies were carried out, and subsequent data argue strongly against the existence of diborane as a kinetically important species in tetrahydrofuran,[16a] thus making the mechanism proposed by Klein and Dunkelblum suspect.
(20) J. Klein and E. Dunkelblum, *Tetrahedron*, **23**, 205 (1967).
(21) L. Melander, "Isotope Effects on Reaction Rates", Ronald Press, New York, N.Y., 1960, p 52.
(22) H. C. Brown, O. H. Wheeler, and K. Ichikawa, *Tetrahedron*, 1, 214 (1957).
(23) D. J. Pasto and F. M. Klein, *J. Org. Chem.*, **33**, 1468 (1968).
(24) The lack of an observable torsional angle effect can also be explained if the rate-determining step involves formation of a π complex between borane and the alkene which then rapidly rearranges to the addition product. The H–T and $^{10}B-^{11}B$ KIE's, however, militate against π-complex formation as being rate determining; however, π-complex formation in a pre-rate-determining step appears likely.[25]
(25) D. J. Pasto, "Solution Reactions of Borane and Substituted Boranes" in "Boron Hydrides", E. Muetterties, Ed., Academic Press, 1975.
(26) H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **85**, 2063 (1963).
(27) S. H. Baur, A. Shapp, and R. E. McCoy, *J. Am. Chem. Soc.*, **75**, 1003 (1953).
(28) A. E. Pope and H. A. Skinner, *J. Chem. Soc.*, 3704 (1963).
(29) R. E. Davis, R. E. Kenson, C. L. Kibby, and H. H. Lloyd, *Chem. Commun.*, 593 (1965).
(30) H. C. Brown and K. Ichikawa, *J. Am. Chem. Soc.*, **84**, 373 (1962).
(31) J. Klein and D. Lichtenberg, *J. Org. Chem.*, **35**, 2654 (1970).
(32) D. C. Wigfield and D. J. Phelps, *J. Am. Chem. Soc.*, **96**, 543 (1974).
(33) W. M. Jones, *J. Am. Chem. Soc.*, **82**, 2528 (1960).
(34) H. C. Brown and D. B. Bigley, *J. Am. Chem. Soc.*, **83**, 3166 (1961).
(35) H. C. Brown, H. I. Schlessiger, and A. B. Burg, *J. Am. Chem. Soc.*, **61**, 673 (1939).
(36) Although the vibrational and bending frequencies of the B–H bond are less than those of the C–H bond in the product, KIE's greater than unity are expected for early transition states in which H transfer has progressed to a minor extent. See, for example, L. Melander, *Acta Chem. Scand.*, **25**, 3821 (1971).
(37) The inverse H–D isotope effect observed by Wigfield and coworkers in the reduction of highly unreactive cyclohexanones with lithium tri-*tert*-butoxyaluminohydride (ref 15) could be due to a late transition state as proposed by the authors or by rate-determining complex formation as described herein.

Time-Resolved Fluorescence Study of Triple Exciplex Formation in 1,3-Dinaphthylpropane and 1,4-Dicyanobenzene

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Abstract: The triple exciplex formation between two naphthyl moieties in 1,3-dinaphthylpropane ($\beta\beta$- and $\beta\alpha$-DNP) and 1,4-dicyanobenzene (DCB) was studied by a nanosecond time-resolved fluorescence spectroscopy. The fluorescence spectrum of a dioxane solution of $\beta\beta$-DNP and DCB in the 380–600-nm region consists of three fluorescence spectra of the intramolecular excimer (λ_{max} ~400 nm, τ = 52 ns), the exciplex (DA)* (~420 nm, 9 ns), and the triple exciplex (DDA)* (~490 nm, 110 ns). The fluorescence lifetimes of these three excited species exhibit no concentration dependence of DCB. From no dependence of the excimer fluorescence lifetime on the DCB concentration, it was concluded that the triple exciplex was not formed from the excimer but formed from the exciplex (DA)*. The structure of the triple exciplex and the mechanism of formation are discussed from the results of the triple exciplex formation in $\beta\beta$- and $\beta\alpha$-DNP. Furthermore, the association and dissociation rate constants in these excited species are discussed in terms of the inter- and intramolecular interactions.

It has been well established that the exciplex is an intermediate of the bimolecular electron donor–acceptor (EDA) interaction in the excited state, and that the exciplex is an intermediate of the photochemical and photobiological transformations. It is also believed that the exciplex consists of the bimolecular or two electronic systems (1:1). The triple exciplex (2:1) formation between two naphthalene molecules and 1,4-dicyanobenzene (abbreviated to DCB) was reported first by Beens and Weller on a steady-state fluorescence spectroscopy.[1] Little is known, however, regarding the mechanism of formation and the structure of the triple exciplex.

On the other hand, the intramolecular excimer and exciplex were reported in several EDA systems in which the electron donor and acceptor moieties were linked by a trimethylene chain. These intramolecular exciplex formations have several advantages in their efficiency and in the decision of their geometrical conformation. Chandross et al.[2]

suggested that the strong geometrical preference is unessential in the exciplex formation in the (naphthalene)–$(CH_2)_3$–(dimethylamine) system. Okada et al.[3] also concluded in the intramolecular system of (anthracene)–$(CH_2)_3$–(N,N-dimethylaniline) that a parallel sandwich structure might be favorable but not necessary for the exciplex formation. Itoh et al.,[4–6] nevertheless, reported that the exciplex (above ~150 K) and the fluorescent EDA complex (below ~120 K) were formed both in the intra- and intermolecular systems of 9,10-dicyanoanthracene and alkylnaphthalenes in the nonpolar solvent, and their experimental and theoretical studies revealed that the exciplex needs geometrically a strong favorable structure.[7] Furthermore, Chandross and Dempster[8] reported strong intramolecular excimer formation in the two symmetrical 1,3-dinaphthylpropanes (abbreviated to $\beta\beta$- and $\alpha\alpha$-DNP), which implies that the stable excimer conformation is the symmetrical sandwich arrangement. On the other hand, Avouris et al.[9]