# STRUCTURES OF THE TRANSITION STATES OF SOME INTERMOLECULAR HYDRIDE TRANSFER REACTIONS

Gerasimos J. Karabatsos* and Michael Tornaritis

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Summary: The large k_H/k_D isotope effects, 7-9, obtained in the hydride transfer reactions of triarylmethanes with triarylmethyl cations support linear rather than nonlinear transition states.

Intermolecular hydride transfers have been depicted in recent years as occurring through nonlinear(I) rather than linear (II) transition states. The first suggestion of a nonlinear transition state for hydride
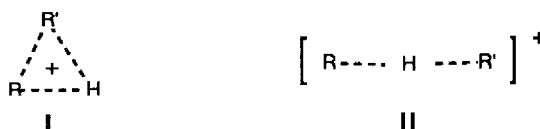

transfer processes was made by Hawthorne and Lewis.[1] In discussing the hydrolysis of pyridine diphenylborane, they stated that "the only reasonable point of attack of an electrophile on a bond to hydrogen must be the center of high electron density, that is, the bond, and a linear configuration A---H---B is not to be expected", and suggested III as the structure of the transition state. Similarly, Olah and his co-workers[2]
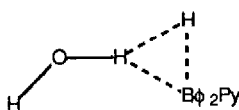

III

have proposed nonlinear structures in reactions of hydrocarbons with carbocations. Theoretical calculations[3] of the structure of protonated ethane, $C_2H_7^+$, have led to the conclusion that the minimum energy structure is IV, where $\theta = 121.7°$.
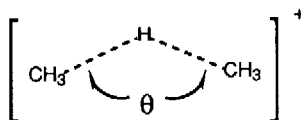
IV

There is no experimental evidence that bears directly on the question of whether I or II is the structure of the transition state of intermolecular hydride transfer reactions. Below we present such evidence .

The magnitude of the kinetic isotope effect k_H/k_D depends[4,5] on the relative values of the force constants f_1 and f_2, and the value of θ. It is maximum when $f_1 = f_2$ and $\theta = 180°$. O'Ferrall has calculated[5] k_H/k_D to

$$A \overset{f_1}{\text{--}\!\text{--}} \overset{(D)}{\underset{\displaystyle \smile_{\theta}}{H}} \overset{f_2}{\cdots} B$$
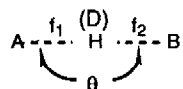
be 7.9 for $\theta = 180°$; 6.2-6.4 for $\theta = 150°$; 3.0-3.9 for $\theta = 120°$; and 1.7-2.3 for $\theta = 90°$. In intramolecular 1,2-hydride shifts of carbocations, where θ is substantially smaller than $180°$ (trigonal transition state), experimental k_H/k_D values range[6] between 1.2-3.3. In intermolecular hydride transfers the reported experimental k_H/k_D values are also small. For example, in the hydrolysis of pyridine diphenylborane and its deuterated analog k_H/k_D was found[1] to be 1.52. Bartlett and Collum[7] obtained $k_H/k_D = 1.84$ when isopropyl alcohol and its α-d analog were oxidized by the triphenylmethyl cation. The small values of these intermolecular isotope effects, however, may be due either to nonlinear transition states or to linear transition states with substantially different[8] force constants ($f_1 \gg f_2$ or $f_1 \ll f_2$).

In order to use the magnitude of k_H/k_D as a probe to elucidate the structures of the transition states of intermolecular hydride transfers, systems must be chosen where f_1 and f_2 are the same or of comparable magnitude. We have chosen triarylmethanes reacting with triarylmethyl cations as systems cogently suited for this purpose.

Table I summarizes k_H/k_D values - - each being the average of several measurements - - for three reactions, at three temperatures. In a typical reaction, $0.3-0.6 \times 10^{-3}$ moles of each reactant, in a 1:1 ratio, would be used in 2-4 ml of acetonitrile-d_3. A Bruker 250 MHz NMR spectrometer was used to study these reactions. The rates were calculated from the integrated areas of the appropriate signals as a function of time.

Table 1. Reactions of Triarylmethanes with Triarylmethyl Tetrafluoroborates in Acetonitrile-d_3.

Reaction	t, °C	k_H/k_D[a]	k_H/k_D[b]
$(p\text{-anisyl})_3CH(D)$			
$+ \phi_3C^+BF_4^-$	22.0 ± 0.2	8.1 ± 0.7	6.6 ± 0.5
"	30.0 ± 0.2	7.4 ± 0.7	7.3 ± 0.2
"	40.0 ± 0.2	7.0 ± 0.3	7.1 ± 0.4
$(p\text{-tolyl})_3CH(D)$			
$+ \phi_3C^+BF_4^-$	25.0 ± 0.2		7.0 ± 0.5
"	30.0 ± 0.2	8.4 ± 0.7	8.8 ± 1.5
"	$40.0+0.2$	8.8 ± 0.5	9.5 ± 0.5
$(p\text{-anisyl})_3CH(D)$			
$+ (p\text{-anisyl})\phi_2C^+BF_4^-$	26.0 ± 0.2	8.6 ± 1.1	10.3 ± 0.7
"	30.0 ± 0.2	9.1 ± 0.6	
"	40.0 ± 0.2	8.9 ± 0.3	9.0 ± 0.2

[a]Reactions were carried out by adding a solution of the triarylmethyl tetrafluoroborate in acetonitrile-d_3 to the triarylmethane. [b]Reactions were carried out by adding a solution of the triarylmethane to the triarylmethyl tetrafluoroborate. We consider the corresponding values obtained by either method (a or b) to be within experimental error of one another.

These signals were: For p-trianisylmethane, 3.68 ppm (p-OCH$_3$); for p-tritolylmethane, 2.22 ppm (p-CH$_3$); for the p-trianisylmethyl cation, 4.05 ppm (p-OCH$_3$); for the p-tritolylmethyl cation, 2.61 ppm (p-CH$_3$); and for the p-anisyldiphenylmethyl cation, 4.19 (p-OCH$_3$). All reactions were relatively slow,[9] with the following being typical rates: k_H = (4.63±0.36)x10^{-5} M^{-1}sec^{-1} for the reaction of p-trianisylmethane with triphenylmethyl tetrafluoroborate at 22°; k_H = (2.83±0.17)x10^{-7} M^{-1}sec^{-1} for the reaction of p-tritolylmethane with triphenylmethyl tetrafluoroborate at 25°; and k_H = (5.02±0.14)x10^{-7} M^{-1}sec^{-1} for the reaction of p-trianisylmethane with p-anisyldiphenylmethyl tetrafluoroborate at 26°. Reactions were followed up to 5-20% completion. All three reactions go to completion, i.e., no reactants are detectable at equilibrium.

To make sure that no competing reactions - - such as hydride transfer to an aryl ring of the cation with subsequent hydrogen rearrangement to the central carbon to give the hydrocarbon - - were contributing to the k_H/k_D values, we followed the reaction of p-trianisylmethane-1-d at 40° with triphenylmethyl tetrafluoroborate to 95% completion. No signal was detected at 5.55 ppm where the methine of triphenylmethane absorbs. We obtained similar results with the other two systems.[10]

The results presented in this paper are consonant with a linear transition state, but not with a nonlinear one.[11] It may very well be that the linearity is imposed by the nonbonded interactions between the six large aryl groups, and that in systems where the nonbonded interactions are small, such as the $C_2H_7^+$ cation, the transition states may be nonlinear.

Notes and References

1.　Hawthorne, M.F. and Lewis, E.S. J. Am. Chem. Soc. 1958, 4296.

2.　Olah, G.A., DeMember, T.R. and Shen, J. J. Am. Chem. Soc. 1973, 95, 4952; Olah, G.A., Mo, Y.K. and Olah, J.A. ibid. 1973, 95, 4939; Olah, G.A., Halpern, Y., Shen, J. and Mo, Y.K. ibid. 1971, 93, 1251.

3.　Raghavachari, K., Whiteside, R.A., Pople, J.A. and Schleyer, P.v.R. ibid 1981, 103, 5649.

4.　Westheimer, F.H. Chem. Rev. 1961, 61, 265.

5.　O'Ferrall, R.A.M. J. Chem. Soc. 1970, B, 785.

6.　Winstein, S. and Takahashi, J. Tetrahedron 1958, 2, 316; Collins, C.J., Rainey, W.T., Smith, W.B. and Kaye, I.A. J. Am. Chem. Soc. 1959, 81, 460; Smith, W.B., Bowman, R.E. and Kuret, T.J. ibid. 1959, 81, 997; Douwes, H.S.A. and Kooyman, E.C. Rec. Trav. Chim. Pays-Bas, 1964, 83, 276; Shiner, Jr., V.J. and Jewett, J.G. J. Am. Chem. Soc. 1965, 87, 1382, 1383; Tichy, M., Hapala, J. and Sicher, J. Tet. Letters 1969, 3739; Karabatsos, G.J., Hsi, N. and Meyerson, S. J. Am. Chem. Soc. 1970, 92, 621; Karabatsos, G.J., Orzech, Jr., C.E., Fry, J.L. and Meyerson, S. ibid. 1970, 92, 606; Nordlander, J.E. and McCrary, T.J. Tet. Letters 1972, 94, 5133.

7.　Bartlett, P.D. and McCollum, J.D. J. Am. Chem. Soc. 1956, 78, 1441.

8.　For an experimental example of the dependence of k_H/k_D on the relative magnitudes of f_1 and f_2 in proton transfer reactions see Longridge, J.L. and Long, F.A. J. Am. Chem. Soc., 1967, 89, 1292.

9.　The identity reaction - - triphenylmethane with triphenylmethyl tetrafluoroborate - - proceeded too slowly to allow good rate measurements. Triphenylmethane-1-^{13}C (50% enriched) equilibrated

with the triphenylmethyl cation after about five months at 25°C, as judged from the relative strengths of the ϕ_3C-H singlet at 5.55 ppm and the $\phi_3{}^{13}$C-H doublet (J_{C-H} = 127.5 Hz).

10. Olah, G.A. and Liang, G. J. Am. Chem. Soc. **1973**, <u>95</u>, 3794 have reported 12-26% nucleophilic attack on the ring atoms of the perdeuterotriphenylmethyl cation by such hydride transfer agents as LiAlH$_4$ (ether solvent), NaBH$_4$ (THF solvent) and cycloheptatriene (SO$_2$ or AsF$_3$-CH$_2$Cl$_2$ solvent). They detected no such attack with trialkylsilanes. Had such an attack occurred in our systems to an extent of 4% or greater, we would have detected it. Also, when we reacted triphenylmethane-1-d with the triphenylmethyl tetrafluoroborate under the conditions specified in footnote 9 above, no signal was detected at 5.55 ppm; nor was such a signal detected when we reacted triphenylmethyl tetrafluoroborate with ϕ_3SiD (it was detected in the reaction with ϕ_3SiH).

11. The experimental errors are too large to evaluate the temperature dependence of the k_H/k_D values.

(Received in USA 25 July 1989)