Kinetic isotope effect for the thermally-induced migration of hydrogen in cyclopentadienes

STEWART MCLEAN, C. J. WEBSTER, AND R. J. D. RUTHERFORD Department of Chemistry, University of Toronto, Toronto 5, Ontario Received November 28, 1968

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The Arrhenius parameters have been obtained for the rearrangement of 5-methylcyclopentadiene by a 1,2-hydrogen migration and for the corresponding rearrangement of 5-methylpentadeuteriocyclopentadiene. The results, taken in conjunction with those reported previously, allow the effect of the methyl group on the rate of hydrogen migration to be assessed. The kinetic isotope effect is of particular interest because the hydrogen transfer takes place through a transition state that is unequivocally non-linear.

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We have previously studied the migration of the C-5 hydrogen in certain appropriately substituted cyclopentadienes and we have shown that a pathway exists by which a thermallyinduced, intramolecular 1,2-hydrogen shift can take place; a study of the kinetics of the rearrangement (e.g. $1 \rightarrow 2$) showed that it had true first order characteristics, and the Arrhenius parameters for the migration process were determined in certain cases (1). Related studies have been made by others (2, 3), and the significance of these results as examples of 1,5-sigmatropic processes was pointed out by Woodward and Hoffmann (4).



A determination of the kinetic isotope effect for the hydrogen migration process would be of considerable value for several reasons. We would like to determine the effect of various substituents on the rate of the migration process, and a knowledge of the rate of hydrogen migration in cyclopentadiene itself would be valuable in establishing a basis of comparison; the degenerate rearrangement in cyclopentadiene itself is, of course, unobservable by the techniques we have used, and it has not been experimentally possible to obtain dependable kinetic results for the derivative involving the smallest possible change, 5-deuteriocyclopentadiene¹ (1). However, Roth

¹We are very grateful to Professor A. G. Harrison and Mr. D. Priddle for carrying out these measurements for us. (3) has been able to study the rate of *deuterium* migration in 5-*H*-pentadeuteriocyclopentadiene, and a knowledge of the kinetic isotope effect for the process would allow his results and ours to be interrelated.

The kinetic isotope effect is also of theoretical interest because the intramolecularity of the hydrogen transfer process unambiguously places certain severe restrictions on the transition state for the reaction. The vast majority of kinetic isotope effects for hydrogen transfer reactions that have been investigated have involved linear transition states with respect to the bond makingbond breaking processes; the predominant contribution to the activation energy has then come from the C-H stretching components that are undergoing change, and although attempts have been made to incorporate bending force constants into calculations (5a) for linear transition states, non-linear transition states with a significant C-H bending component appear to have been considered in only a few special cases (5b). In contrast, the hydrogen migration in cyclopentadienes requires unequivocally a non-linear transition state in which the C-H bending component is important, and, in fact, the rearrangement can be viewed as the result of an exaggerated C-H bending vibration. For the rearrangement of cyclopentadiene itself, provided that no metastable intermediate is implicated, the transition state must be symmetrical, with the hydrogen equally bonded to the migration origin and the migration terminus. Furthermore, it appeared reasonable to assume at the start that the distortion of this symmetry in the 5-methylcyclopentadiene case, would have a minimal effect on the characteristics of the transition state.

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Unfortunately, one further modification had to be introduced into the system in order to make the study of the kinetic isotope effect for the 5-methylcyclopentadiene case experimentally feasible. It was not possible to develop a synthesis of 5-methyl-5-deuteriocyclopentadiene and we had to be content to use 5-methylpentadeuteriocyclopentadiene (1-D), which is readily available from cyclopentadiene- d_6 . The second order effects of the 4 extra deuterium atoms could not be determined and the assumption was made that their combined effect would be small relative to the primary effect associated with the migrating atom.

In our first experiments we simply used the technique we have previously described (1) to monitor the decay of the methyl signal of 5methylcyclopentadiene (1-H) and its deuterio derivative (1-D) while each was maintained at a fixed temperature in the probe of the nuclear magnetic resonance (n.m.r.) spectrometer. The $k_{\rm H}/k_{\rm D}$ values obtained varied over a range that was greater than that of the expected experimental error and we decided that it would be necessary to have more precise temperature control and calibration than the variable temperature probe affords. We then used a technique in which the reaction was carried out in a thermostatted bath and then quenched by rapid cooling; the progress of the reaction was then determined from the area of the 5-methyl signal measured in an n.m.r. spectrometer with the probe temperature set low enough that no appreciable further rearrangement of the sample could take place. In this way we were able to study the rearrangement over the temperature range most suitable for each (5-25° for 1-H and 20-40° for 1-D). Table I shows the values obtained for $k_{\rm H}$ (migration), the average value for the (statistically-corrected) rate constant for the hydrogen migration process itself, and the rate constant, $k_{\rm H}$ (decay), for the process actually measured, the decay of the 5-methyl signal in 1-H. The corresponding values for 1-D are shown in Table II, and in Table III these values are corrected for the presence in 1-D of incompletely deuteriated material. The correction was based on the isotopic dilution of the C₅D₆ precursor, determined mass spectrometrically, and assumed that the methyl group entered the molecule in a random fashion; the value obtained in this way for the isotopic dilution of 5-D-5-methyl species is probably an upper limit.

TABLE I					
Rate constants	for	migration	of hydrogen		

 (°С)	$k_{\rm H}({\rm decay})$ (s ⁻¹ × 10 ⁵)	Standard deviation*	$k_{\rm H}$ (migration) (s ⁻¹ × 10 ⁵)
6.1	3.785 3.815	0.032 0.041	1.90
9.8	6.044 5.975	$0.035 \\ 0.055$	3.01
14.4	10.61 10.32	0.13 0.07	5.24
19.5	21.33 20.85	0.78 0.30	10.6
25.1	36.82 36.65	0.41 0.34	18.4

*Based only on the slope obtained by a least squares treatment of the kinetic data and assuming first order kinetics.

TABLE II Rate constants for migration of deuterium (uncorrected for effect of isotope dilution)

<i>T</i> (°C)	$k_{\rm D}({\rm decay})$ (s ⁻¹ × 10 ⁵)	Standard deviation*	$k_{\rm D}$ (migration) (s ⁻¹ × 10 ⁵)
19.5	3.385 3.139	0.241 0.073	1.63
25.1	6.584 6.780	0.080 0.064	3.34
30.1	12.79 12.37	0.19 0.07	6.29
35.1	22.84 22.15	0.48 0.28	11.2
40.1	40.75 39.89	0.23 0.30	20.2

*Based only on the slope obtained by a least squares treatment of the kinetic data and assuming first order kinetics.

TABLE III

Rate constants for migration of deuterium (corrected for effect of isotope dilution)

Т (°С)	$k_{\rm D}({\rm decay})$ (s ⁻¹ × 10 ⁵)	Standard deviation*	$k_{\rm D}$ (migration) (s ⁻¹ × 10 ⁵)	
19.5	3.179 3.003	0.203 0.071	1.55	
25.1	6.322 6.484	$0.063 \\ 0.037$	3.20	
30.1	12.26 11.96	0.15 0.05	6.05	
35.1	21.82 21.37	0.32 0.22	10.8	
40.1	39.21 38.34	0.20 0.23	19.4	

*Based only on the slope obtained by a least squares treatment of the kinetic data and assuming first order kinetics.

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Comparison of the results recorded in Table I with those we obtained previously (1) reveals a significant difference between the two sets of figures for the values of $k_{\rm H}$ (migration) at each temperature. This difference, which has caused us some concern, probably arises from a systematic error in one of the sets of figures; in our earlier work (1) we depended on the calibration of the variable temperature probe, while in the present investigation our technique has allowed a much higher degree of precision in the determination of the reaction temperature, and consequently we believe that our present results are the more dependable and the temperatures recorded previously were 4-5° too low. In agreement with this, the Arrhenius plot of our present results gave a good straight line, the slope of which was the same, within the expected limits of accuracy, as that obtained in the earlier study. Our present results correspond to:

 $k_{\rm H}({\rm migration}) = (7.49 \times 10^{10}) \, {\rm exp}$

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$$(-19.930/RT)$$
 s⁻

 $E_{\rm a} = 19.9$ kcal/mole (standard

deviation 0.3)

 ΔS^{\pm} (300 °K) = -10.8 e.u. (standard

deviation 1.0)

Comparison of the results in Tables II and III shows that slightly better first order kinetic plots were obtained when the correction for isotope dilution was applied. The differences between the two sets of figures are, in fact, within the expected limits of error for this technique, and this serves to confirm our supposition that our material was of sufficient isotopic purity. When each set of kinetic data was plotted separately, there was very little difference in the Arrhenius parameters obtained, but the standard deviations of slope and intercept were very slightly lower in the corrected case. We choose, therefore, to report the results obtained from Table III which are:

 $k_{\rm D}({\rm migration}) = (7.58 \times 10^{11}) \exp$

 $(-22 \ 350/RT) \ s^{-1}$

 $E_{\rm a} = 22.35$ kcal/mole (standard

deviation 0.1)

 ΔS^{+} (300 °K) = -6.2 e.u. (standard

deviation 0.3)

It can be seen that the Arrhenius activation

energy for deuterium migration is greater than that for hydrogen migration, but the entropy of activation is less negative for deuterium; from these results it follows that the free energy of activation for deuterium migration is higher by about 1.1 kcal mole⁻¹ in the temperature range studied. The values for $k_{\rm H}/k_{\rm D}$, calculated from the Arrhenius plot, show a substantial temperature dependence, being 7.67 at 7 °C, 5.75 at 27 °C, and 4.45 at 47 °C; the isokinetic temperature is 253 °C, calculated by extrapolation and with the assumption that the Arrhenius plots are linear through the whole range.

It is clear from a comparison of our present results with those of Roth (3) that, as we had previously suggested (1), the 5-methyl group appreciably lowers the activation energy for the migration of the hydrogen from C-5, leading to an increase in the rate of rearrangement. The 1-methyl isomer (with methyl at sp^2 carbon) is appreciably more stable than the 5-methyl isomer (with methyl at sp^3 carbon) (1); it is probable that the methyl group in the first isomer has a stabilizing effect relative to the unsubstituted case and it is possible that the methyl group has the opposite effect in the second case. The lowering of the activation energy for the rearrangement of 5-methylcyclopentadiene may reflect both influences, one raising the ground state and the other lowering the transition state energy. It seems probable in any case that the transition state is appreciably affected by the stabilizing influence of the methyl group at the incipient sp^2 carbon center, and to this extent the approximation made earlier that the distortion of the symmetry of the transition state by the methyl substituent could be neglected is inaccurate, but it is difficult to place this on a quantitative basis with any confidence. The stabilization of the 1-methyl isomer with respect to the 5-methyl isomer (from equilibrium studies (1)) and the lowering by the methyl group of the activation energy for hydrogen migration (from the kinetic comparison of substituted and unsubstituted cyclopentadienes) are both about 2 kcal/mole, indicative that the major part of the effect that the methyl group has in the product is already felt in the transition state. However, the equilibrium values are recognized to be only very approximate and the activation energy figures are based on the difference between our results and those of Roth (3), both of which have probable error limits that are appreciable relative to the difference.

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Because measurements were made on 1-H and 1-D under conditions that were as nearly identical as possible, the phenomenological aspects of the study of the kinetic isotope effects can, we feel, be accepted with some confidence. The range of $k_{\rm H}/k_{\rm D}$ values is not unusual and the rate differences can be traced to both enthalpy and entropy factors. However, because we have not been able to separate primary and secondary isotope effects and because of the difficulties already outlined regarding the nature of the transition state, we do not feel that it is appropriate at this time to do more than comment briefly on the theoretical significance of the results. The important feature of this rearrangement is the non-linearity of the transition state; the difference in activation energy between the hydrogen and the deuterium cases could be attributed to the complete loss in the transition state of one bending mode (near 1360 cm⁻¹ for C-H) and smaller contributions from other modes, but we have not followed this approach any further than the observation than any meaningful calculation will require consideration of a more extensive portion of the molecule and its associated vibrational modes. The extent of tunneling is another question of considerable interest here (and it may be noted that proton tunneling in "Woodward-Hoffmann forbidden" cases is a question of further interest); the ratio of preexponential factors we have determined $(A_{\rm H}/A_{\rm D})$ ~ 0.1) has a value that has been considered evidence for an appreciable degree of tunneling (5c), but we recognize that our data have been obtained over a restricted temperature range only and the evidence is therefore suggestive rather than definitive.

Experimental

A Varian A-60 nuclear magnetic resonance (n.m.r.) spectrometer equipped with a variable-temperature probe was used. Analyses of isotopic composition were carried out directly by mass spectrometry using an AEI MS902.¹

Cyclopentadiene-d₆

A solution of NaOD in D_2O , prepared by the reaction of Na₂O₂ (5.0 g) with D_2O (33.0 g), was vigorously stirred for 1 h at 0° in an atmosphere of nitrogen with cyclopentadiene (12.0 g) and 25 ml dimethyl sulfoxide. When the mixture was allowed to settle, three layers separated. The upper layer was partly deuteriated cyclopentadiene (62 atom % D) and the lower layers were dimethyl sulfoxide and partly exchanged D_2O (which could be recovered by distillation and used again in a preliminary treatment of another sample of cyclopentadiene). When the partly deuteriated cyclopentadiene





was taken through another two cycles of this process, the composition of the product typically obtained was: C_5D_6 , 82.3; C_5D_5H , 15.3; $C_5D_4H_2$, 1.9; less highly deuteriated species 0.5 (95.6 atom % D).² Material of at least this isotopic purity was converted to 5-methylpentadeuteriocyclopentadiene by the method described previously for cyclopentadiene itself (6).

Kinetic Measurements

The reaction vessel shown in Fig. 1 was constructed from thin copper sheet. Reactants were introduced from a syringe which was adapted to fit the glass joint, and, when a sample was required, a measured volume could be forced through the copper tube, to which was connected

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²This method was developed in this laboratory by Mr. T. F. W. McKillop and we are very appreciative of the experimental skill that he demonstrated in doing so. Under the conditions used here virtually no deuteriation of the DMSO takes place (on the basis of the mass spectrum of recovered DMSO); the rate of base-catalyzed hydrogen exchange in DMSO is known to be strongly dependent on the composition and nature of the reaction medium and it is interesting to note that, under prescribed conditions, the DMSO – D_2O – NaOD system can be used to prepare DMSO- d_6 rapidly and efficiently (7).

a piece of flexible Teflon tubing, by a pumping action of the syringe.

The reaction vessel containing 8 ml of a 4% solution of hexamethyldisiloxane in carbon tetrachloride was placed in a thermostatted bath $(\pm 0.02^{\circ})$ and, when thermal equilibrium was established, the substituted cyclopentadiene (2 ml) was added and thoroughly mixed with the solvent by agitation of the reaction vessel. Aliquots were withdrawn at measured intervals and collected in chilled n.m.r. sample tubes, which were then immediately placed in a mixture of dry ice and acetone and stored there until they could be examined in an n.m.r. spectrometer with a probe temperature of -20° . Peak areas were then measured by electronic integration after optimum instrumental conditions had been established. The area of the 5-methyl peak was measured relative to that of (a) the hexamethyldisiloxane signal and (b) the total methyl signal of all methylcyclopentadienes.

The data obtained were analyzed by a standard least squares routine using an IBM 7094 computer to obtain first order rate constants. The values obtained from areas as a fraction of the total methyl signal gave more consistent results and these are reported in Tables I and II. Arrhenius parameters were obtained by the corresponding least squares analysis. Corrections for the effects of isotope dilution were made on the assumption that the methylation reaction replaced hydrogen or deuterium in the precursor cyclopentadiene in a random manner; thus 5-methyl-5-H species would be formed from 1/6 of the C_5D_5H molecules, 1/3 of the $C_5D_4H_2$ molecules, and so on. The typical deuteriated cyclopentadiene described above would then lead to 3.5% 5-methyl-5-H species in the product. The actual concentration of 5-methyl-5-D species at time t, D(t), was calculated from

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the apparent concentration S(t) based on the 5-methyl n.m.r. signal and the concentration of 5-methyl-5-H species, H(t), which in turn was calculated from the above fractions and the value of $k_{\rm H}$ (decay) obtained from the Arrhenius plot.

$$D(t) = S(t) - H(t) = S(t) - H(0) \exp(-k_{\rm H}t)$$

Rate constants calculated from these corrected values are reported in Table III.

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- S. MCLEAN and P. HAYNES. Tetrahedron Letters, 2385 (1964); Tetrahedron, 21, 2329 (1965).
 V. A. MIRONOV, E. V. SOBOLEV, and A. N. ELIZAROVA. Tetrahedron, 19, 1939 (1963).
 W. R. ROTH. Tetrahedron Letters, 1009 (1964).
 R. B. WOODWARD and R. HOFFMANN. J. Am. Chem. Soc 87, 2511 (1965)
 (a) R. F. W. BADER. Can. J. Chem. 42, 1822 (1964). R. A. M. O'FERRALL and J. KOUBA. J. Chem. Soc. B, 985 (1967). 985 (1967)
 - (b) M. F. HAWTHORNE and E. S. LEWIS. J. Am. Chem.
 (b) M. F. HAWTHORNE and E. S. LEWIS. J. Am. Chem.
 Soc. 80, 4296 (1958). V. J. SHINER, JR. and J. G.
 JEWETT. J. Am. Chem. Soc. 87, 1382 (1965).
 (c) R. P. BELL. The proton in chemistry. Methuen and Co., Ltd., London. 1959. p. 211.
 S. MCLEAN and P. HAYNES. Tetrahedron, 21, 2012 (1965).
- 6.
- 2313 (1965). E. BUNCEL, E. A. SYMONS, and A. W. ZABEL. Chem. Commun. 173 (1965). 7.