Deductions from Small Primary Deuterium Isotope Effects

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Received February 5, 1962

With reasonable assumptions, primary deuterium isotope effects of small magnitude can be used in conjunction with calculations to show whether the transition state is product-like or reactant-like.

The deuterium isotope effect on an equilibrium can be calculated with good accuracy from the observed vibrational transitions of the deuterated and nondeuterated forms of both reactants and products. This is contrary to the situation for transition states, whose spectra cannot be measured. It was of interest to see if these equilibrium isotope effects would yield any information about transition state structure. With reasonable assumptions, the equilibrium isotope effect together with the measured kinetic isotope effect for certain hydrogen-transfer reactions does indeed tell whether the transition state is closer in structure to reactants or to products.

It has recently been emphasized that the primary deuterium isotope effect can be of nearly any magnitude, depending on the force constants of the transition state relative to those of the reactant.[1] If the transition state has force constants exactly like those of the reactants, the kinetic isotope effect k_H/k_D is 1.00. If the transition state has force constants exactly like those of the products, k_H/k_D is the same as the equilibrium isotope effect K_H/K_D for the reaction. If the XH and HY force constants of the transition state X- - - H - - - Y are equal, k_H/k_D has some maximum value of 7 or more.[1] Since the periodic stretching vibration of the transition state is the major factor in determining the kinetic isotope effect, and since the stretching zero-point energy difference between X---H---Y and X---D---Y drops rapidly as the force constants become equal, it is reasonable to assume that the kinetic isotope effect would undergo a monotonic increase to its maximum value and then a monotonic decrease, if the structure of the transition state were changed from being reactant-like to being product-like. This assumption seems reasonable because, if the periodic stretching frequencies are called ν_H and ν_D, then *both* ν_H and ν_H/ν_D become considerably smaller as the transition state becomes symmetrical (equal force constants). The fact that the reduced mass for the vibration must become larger lowers ν_H, and ν_H/ν_D must, of course, approach 1.00 as the hydrogen atom moves less and less in the periodic stretching vibration. Therefore, barring some exceedingly large increase in the *bending* vibrations of the transition state relative to the reactant, the effect of the stretching vibration should predominate and the assumption should be quite sound.

On the basis of the above assumption the following conclusion can be drawn: *The kinetic isotope effect must always be greater than K_H/K_D if the transition state structure is on the product side of symmetrical.* Therefore, if K_H/K_D were, say, 1.5 and k_H/k_D were 1.2, the transition state for the reaction must in reality be closer to reactants than to products.

If, on the other hand, K_H/K_D were less than 1.00 and k_H/k_D were also quite a bit less than 1.00, the transition state must be closer to products than to reactants.

There are two straightforward cases to which this concept can be applied. In the abstraction of hydrogen atoms from toluene and deuterotoluenes by chlorine atoms, $k_H/k_D = 1.34 \pm 0.04$ at 77° in carbon tetrachloride solution.[2] Using the usual expressions for isotope effects[3] and making the following assumptions K_H/K_D can be calculated. For the C—H and C—D bonds of benzyl radical it was assumed[4] that $\nu_{CH} = 2900, 1400, 900$ cm.$^{-1}$ and $\nu_{CH}/\nu_{CD} = 1.35$, and that the deuterium substitution in such a heavy molecule has a negligible effect on the translations and moments of inertia. For HCl and DCl the single vibrations were taken at 2886 and 2070 cm.$^{-1}$, respectively,[5] and the contributions of translation and rotation (not negligible for light molecules) were included. The frequencies for toluene itself cancel for an *intramolecular* isotope effect K_H/K_D was calculated to be 1.54 at 77°. The neglected moments of inertia should *increase* this value by about 10%. It is concluded that the transition state for this reaction is *closer to reactants* than to products since $k_H/k_D = 1.34$ is less than $K_H/K_D = 1.54$.

In the reaction of Ph_3SiH and Ph_3SiD with base and water in piperidine solvent, $k_H/k_D = 1.15$ at

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[1] F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

[2] K. B. Wiberg and L. H. Slaugh, *J. Am. Chem. Soc.*, **80**, 3033 (1958).

[3] L. Melander, "Isotope Effects on Reaction Rates," Ronald Press Co., New York, N. Y., 1960, Chap. 2.

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, New York, N. Y., 1958, pp. 34 ff. These frequencies are based on a methylene group.

[5] G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed., D. Van Nostrand Co., Princeton, N. J., 1950, p. 534; the frequency of the first vibrational transition in the infrared was used, $\nu = \omega_e - 2\omega_e x_e$. The frequency of the deuterium molecule was taken to be the frequency of the protium molecule divided by the square root of the calculated reduced mass ratio.

25°.[6] In this case hydrogen is being transferred from silicon to another hydrogen atom from the solvent to produce H—H or D—H as product. For SiH and SiD bonds the stretching frequencies were taken as[6] 2135 and 1547 cm.$^{-1}$, respectively. The bending frequencies were taken as $\nu_H = 978$, 910,[7] and $\nu_H/\nu_D = 2135/1547 = 1.38$ was assumed for the bending frequencies. Frequencies of 4159 and 3627 were taken for HH and DH.[8] The translations and moments of inertia were neglected for SiH *vs.* SiD but included for HH *vs.* DH. K_H/K_D was calculated to be 1.7 at 25°. The transition state of this reaction must have the hydrogen atom which is being transferred closer to the reactants than to the products, since k_H/k_D is considerably less than K_H/K_D.

In reactions such as enolization or E2 elimination (the transfer of hydrogen from C to the O of HO$^-$), K_H/K_D was calculated to be about 0.9, using the previous values for the CH and CD frequencies and the known partition functions for water.[9] For CH being changed to $\begin{smallmatrix}\diagdown & \\ & \mathrm{O}^{+}\text{—H} \\ \diagup & \end{smallmatrix}$ by attack of water (*e.g.* in enolization), K_H/K_D was calculated to be about 1.3.

For the reaction of bromine atoms with toluene, K_D/K_H was calculated to be 1.83 but $k_H/k_D = 4.9 \pm 0.3^2$ so no information is obtained. The vibration of HBr was used[10] together with the theoretical reduced mass to calculate the frequency of DBr, and translations and rotations were allowed for. However, it has already been concluded that the transition state for the abstraction of a hydrogen atom from toluene by a chlorine atom is closer to reactants than to products. The fairly large isotope effect for abstraction by bromine means that the transition state is *closer to products* than for chlorine. This is in accord with a recently proposed rule[11] for predicting effects of structural changes in reactants on the structure of transition states, since chlorine is predicted to lengthen the Cl---H bond and shorten the H---C bond relative to bromine. It is the first time the rule has been checked for a free radical reaction.

The results presented here are somewhat qualitative because the numbers used in calculating K_H/K_D were guessed at. Quantitative information can be obtained, however, by examining the spectra of deuterated and nondeuterated reactants and products. *All* isotopic frequency shifts can then be accounted for. Therefore, this approach offers a way of *analyzing the structure of some transition states by means of observable quantities.*

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[6] L. Kaplan and K. E. Wilzbach, *J. Am. Chem. Soc.*, **77**, 1300 (1955).

[7] G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Princeton, N. J., 1945, p. 167 (SiH_4).

[8] Ref. 5, p. 532.

[9] C. G. Swain, R. F. W. Bader, and E. R. Thornton, *Tetrahedron*, **10**, 200 (1960). The square root of the ratio for H_2O *vs.* D_2O was used.

[10] Ref. 5, p. 534.

[11] C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **84**, 817 (1962).

Extension of the Hammett Equation to Photochemical Quantum Yields

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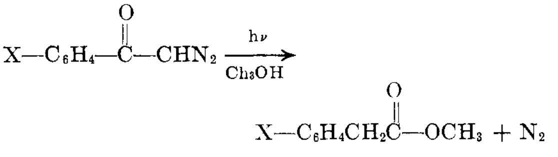
Received August 7, 1961

The quantum yields of a series of substituted diazoacetophenones have been correlated with the effects of substituents by means of the Hammett equation. A possible rationalé for this is discussed in terms of the excited state from which reaction occurs.

Recent interest in organic photochemistry has resulted in detailed studies of the mechanisms and quantum yields (molecules reacted per quantum absorbed) of many reactions,[1] although there seems to have been only one systematic study[2] of the effect of substituents on an aromatic ring on quantum yields in a photochemical reaction. In this study Kirmse and Horner[2] irradiated a series of substituted diazoacetophenones at their principal absorption maxima (approx. 290 mμ) and determined the quantum yields of the reaction. Since these quantum yields vary over a rather wide range, they permit *a test of the hypothesis that these variations are dependent on the resonance and inductive effects of the substituents.*



$$X\text{—}C_6H_4\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CHN_2 \xrightarrow[CH_3OH]{h\nu} X\text{—}C_6H_4CH_2\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OCH_3 + N_2 \quad (1)$$

The electronic effects of substituents in aromatic rings have been correlated with the nature of the substituents by means of the Hammett equation:

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[1] W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., 1941, Appendices.

[2] W. Kirmse and L. Horner, *Ann.*, **625**, 34 (1959).