

## The Ordering of Carbon-Hydrogen Bond Strengths using Isotope Effects

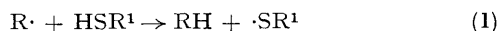
By EDWARD S. LEWIS\* and MURDOCK M. BUTLER

(Department of Chemistry, Rice University, Houston, Texas 77001)

**Summary** Variations in the tritium isotope effects in the radical addition of  $R^1SH$  to  $R^2R^3C=CH_2$  are interpreted in terms of the transition state symmetry, measured by the difference in bond strengths to hydrogen in the initial state ( $R^1S-H$ ) and the final state ( $H-CR^2R^3CH_2SR^1$ ).

THE increase in hydrogen isotope effects to a maximum as the transition state becomes symmetric is well established in theory<sup>1,2</sup> and practice.<sup>3,4</sup> The use of  $\Delta pK_a$  as a measure of transition state symmetry in proton transfers leads to a roughly defined maximum with  $\Delta pK_a$  near zero.<sup>3,5</sup> The roughness can, in part, be attributed to the difference in solvation between the transition state and the acids and bases at equilibrium.

We report some isotope effects in the atom-transfer reaction (1).  $R\cdot$  is of the form  $\cdot C(CH_2SR^1)R^2R^3$  and the



overall reaction is the radical chain addition of  $R^1SH$  to  $R^2R^3C=CH_2$ . The results are understandable if  $D_{RH} - D_{SH}$ , the difference in the bond strengths in the reagent and product in reaction (1), is a good measure of the transition-state symmetry.

The olefin was heated with bisazoisobutyronitrile and a tenfold excess of the mercaptan which had previously been exchanged with tritiated water. After several half-lives of the initiator decomposition, the addition product ( $R^2R^3CHCH_2SR^1$ ) was isolated, purified, characterized by n.m.r. and often by oxidation to the sulphone, and counted

by solution scintillation methods. The ratio of the (efficiency corrected) molar specific activity of the mercaptan to that of the product sulphide gave the isotope effect (a correction 3–4% allowed for the finite excess of mercaptan). The isotope effects, which we believe to be correct to better than  $\pm 5\%$ , are presented in the Table.

*Tritium isotope effects in the addition of  $R^1SH$  to  $R^2R^3C=CH_2$  at 70°*

$R^2$	$R^3$	$k_H/k_T$ ( $R^1=Ph$ )	Order	$k_H/k_T$ ( $R^1=PhCH_2$ )
PhCH <sub>2</sub> .. ..	H	2.61	1	4.81
N-Carbazolyl .. ..	H	2.68	1	4.44
OAc .. ..	H	2.67	1	5.75
CO <sub>2</sub> Me .. ..	H	3.89	2	8.04
CO <sub>2</sub> Me .. ..	Me	4.42	3	9.75
CN <sup>+</sup> .. ..	H	4.96 <sup>b</sup>	4	7.75 <sup>b</sup>
<i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> .. ..	H	5.29 <sup>a</sup>	5	10.8
Ph .. ..	H	5.75 <sup>a</sup>	6	9.94
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> .. ..	H	5.99 <sup>a</sup>	7	9.34
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> .. ..	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	7.02	8	8.13
Ph .. ..	Ph	5.76 <sup>a</sup>	9	6.70
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> .. ..	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	4.68 <sup>a</sup>	10	— <sup>c</sup>

<sup>a</sup> At 80°. <sup>b</sup> These isotope effects may be those for an ionic process rather than reaction (1). <sup>c</sup> No product isolated; 1,1-di-*p*-anisylethylene was recovered.

The large range of isotope effects is noteworthy, but there are some strange features. Thus, the isotope effect with thiophenol correlates with the Hammett  $\sigma$ , but  $\rho$  has the

opposite sign with substituted styrenes and with substituted diphenylethylenes. Considering first only the results with thiophenol, these anomalies are neatly accommodated by assuming that the SH bond strength in thiophenol falls between the CH bond in the product with  $R^2 = p\text{-MeOC}_6\text{H}_4$ ,  $R^3 = \text{H}$  and that with  $R^2 = R^3 = p\text{-ClC}_6\text{H}_4$ . Assuming that only the arylated systems might have a CH bond weaker than the SH bond, and that a maximum isotope effect is expected when  $D_{\text{SH}} = D_{\text{RH}}$ , we can assign the order of decreasing  $D_{\text{RH}}$  given in the Table.

$\text{PhCH}_2\text{SH}$  has a stronger SH bond than thiophenol<sup>6</sup> and would, therefore, be expected to give different isotope effects. The Table shows that the isotope effect with  $\text{PhCH}_2\text{SH}$  also follows the order derived from the thiophenol

isotope effects, except with acrylonitrile, for which an ionic mechanism is likely.<sup>7</sup> The maximum isotope effect falls at an earlier position in the order, as expected. The failure of di-*p*-anisylethylene to react is consistent with the presence of an endothermic step in the chain.

Some of the isotope effect variation may be due to tunnelling, which is maximized with a symmetric transition state,<sup>2</sup> some may be connected with variable contributions of ionic structures of the transition state with changes in  $R^2$  and  $R^3$ , and some may be connected with a variation in the CHS angle in the transition state,<sup>8</sup> but the simplest explanation is that based on the change in bond strengths.

We thank the Robert A. Welch Foundation for support.

(Received, May 10th, 1971; Com. 724.)

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