Acknowledgment. We acknowledge gratefully support of this research by a grant from the Robert A. Welch foundation.

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Isotope Effects in Hydrogen Atom Transfer. VII. Benzylic Hydrogen Abstraction by *tert*-Butoxy and Other Radicals

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Received June 6, 1975

Abstract: Chlorination of toluene by *tert*-butyl hypochlorite involves the attack of *t*-BuO· on the benzylic hydrogen; isotope effects can be measured by comparing the activity of the product *t*-BuOH with that of PhCH$_3$-*t*. At 40 °C, $k_H/k_T = 11.5$; substituted toluenes give similarly rather large values of k_H/k_T, which increase slightly with σ. In contrast, Cl· attack gives $k_H/k_T = 3.7$, in rough agreement with earlier deuterium effects. Literature values for the isotope effect in the nearly equally exothermic attack by CH$_3$· and the more exothermic attack by C$_6$H$_5$· are closer to the *t*-BuO· value than to the Cl· value. Earlier large values of isotope effect in bromination are confirmed with tritium. Secondary effects of tritium in the *t*-BuO· attack were measured, and are undetetable. It is postulated that the symmetry effect on the isotope effect is important only when one of the elements flanking hydrogen in the transition state is in the second row or beyond.

Earlier papers[1] in this series have considered the isotope effect in hydrogen atom transfers as it is influenced by bond dissociation energy or ΔH factors, which show, in agreement with Pryor and Kneipp,[2] that large isotope effects are associated with near zero values of ΔH. Extension to the much more exothermic reactions of aryl radicals with thiols showed the expected very small isotope effects, but also showed small substituent effects which were most easily interpreted in terms of a polar transition state.[3] We now concern ourselves with hydrogen atom transfers between carbon and other elements, especially with the transfer to the *tert*-butoxy radical.

Toluene is chlorinated by *tert*-butyl hypochlorite in a radical chain reaction where we shall be concerned with step 1. Various methods can in principle be used. The use of

$$(CH_3)_3CO\cdot + H_3CPh \rightarrow (CH_3)_3COH + \cdot H_2CPh \quad (1)$$

tritium as the hydrogen isotope puts further limitations on the methods that can be used; for example, Wiberg and Slaugh[4] measured an intramolecular isotope effect by chlorinating PhCHD$_2$ or PhCH$_2$D, and determining the D content of the benzyl chloride. With trace label tritium the T content of the benzyl chloride is virtually independent of the primary isotope effect until the extent of chlorination is quite large, and the method is quite unsuitable, especially since dichlorination can occur at large conversions. We determined the T content of the Me$_3$COH, avoiding problems of exchange and adsorption by dilution with a large excess of water, and counting the water solution. This method does not count methane derived from methyl radicals from the decomposition of the *tert*-butoxy radicals, since it is not water soluble. It does count HCl, which is the product from the chlorine atom chain which sometimes accompanies reaction 1 in the hypochlorite reaction. We therefore added trichloroethylene to stop these chains, following the method of Zavitsas and Pinto,[5] and the success of this technique is demonstrated by the very different effects in chlorination with the hypochlorite and with chlorine.

The same method was used to measure the isotope effects in the chlorination of some substituted toluenes with *tert*-butyl hypochlorite, and in the reaction of chlorine and bromine with toluene. The results are presented in Table I.[5b] The table also includes some deuterium isotope effects measured from the isotopic composition of benzyl chloride made from a mixture of toluene and toluene-α-d_3. The two measures are in reasonable accord, as shown by values of k_H/k_T calculated from the deuterium isotope effects.[6] The rather large discrepancy for Cl· attack is troublesome, although it does not affect any arguments. We have more confidence in the tritium value, but in any case the results overlap within less than three standard deviations, and the Swain–Schaad equation is least accurate for small isotope effects.

The isotope effects with *tert*-butoxy radical are strikingly larger than those with chlorine atoms. A conceivable systematic error arising from our calculation of specific activity of *tert*-butyl alcohol exists, but can be shown to be unimportant. This calculation includes the assumption that the yields of benzyl chloride and *tert*-butyl alcohol are the same. If the yield of alcohol, which is required to get the specific activity, were much smaller than that of the chloride, then our activities would be too small, and the isotope effects correspondingly high. It might be imagined that reactions 2 and 3 contribute heavily to the yield of benzyl chloride, without producing any *tert*-butyl alcohol, and thus produce this systematic error. However, under our conditions (ca. 0.8 to 2 M toluene) we estimate that not more than about 20% of the *tert*-butoxy radicals undergo reaction 2,[7] and that of the methyl radicals produced, virtually none undergo reaction 3, which has an activation energy of greater than 7 kcal;[8] instead they react with *tert*-butyl hypochlorite, with an activation energy less than 4.2 kcal.[9] This is consistent with the earlier claim that the exclusive fate of all alkyl radicals is to react with *tert*-butyl hypochlorite,[10] and these authors in fact showed (under conditions of far more extensive reaction 2) that the *tert*-butyl alcohol yields were somewhat higher than the alkyl chloride yields.

$$(CH_3)_3CO\cdot \rightarrow (CH_3)_2C{=}O + CH_3\cdot \qquad (2)$$

$$CH_3\cdot + HCH_2Ph \rightarrow CH_4 + \cdot H_2CPh \qquad (3)$$

The rather small substituent effect with the substituted toluenes deserves some minor comment. The isotope effect increasing with the Hammett σ is in the expected direction, no matter what the source of the substituent effect is. The isotope effect would from the symmetry effect be largest for the least exothermic case[1,7] and very likely the breaking bond would be strongest with *m*-chlorotoluene. However, contribution of polar structures, in the direction

$$\overset{\delta-}{t\text{-BuO}}\text{- - H - -}\overset{\delta+}{CH_2Ar}$$

would be greatest with Ar = *p*-tolyl, which would lead to the smallest isotope effect in this case.[3] We can therefore not distinguish between these alternate explanations of substituent effects, nor because of possible small substituent dependent systematic errors can we make firm quantitative use of this variation with substituent.

Table I. Isotope Effects for $X\cdot + HCH_2Ar \rightarrow XH + \cdot CH_2Ar$ at 40 °C

X	Ar	k_H/k_T[a]	k_H/k_D[b]
$Me_3CO\cdot$	*m*-ClC_6H_4	14.6 ± 1.5	
$Me_3CO\cdot$	*p*-ClC_6H_4	12.7 ± 1.1	
$Me_3CO\cdot$	C_6H_5	11.5 ± 0.5 (11.4 ± 1.2)	5.4 ± 0.4
$Me_3CO\cdot$[c]	C_6H_5[c]	18.8 ± 0.6[c]	
$Me_3CO\cdot$	*m*-MeC_6H_4	11.4 ± 1.0	
$Me_3CO\cdot$	*p*-MeC_6H_4	10.6 ± 0.4	
Br·	C_6H_5	14.0 ± 0.8 (15.5 ± 1.3)	6.7 ± 0.4
Cl·	C_6H_5	3.7 ± 0.2 (2.3 ± 0.4)	1.8 ± 0.2

[a] Competitive tritium isotope effects based on counting HX in water. The indicated errors are standard deviations of the means of two to five runs. Numbers in parentheses calculated from the last column. [b] Competitive on mixture of $C_6H_5CH_3$ and $C_6H_5CD_3$ from D content of $C_6H_5CH_2Cl$ or Br. [c] Measured at 0 °C rather than 40 °C. The two points fit $k_H/k_T = 2.5 \exp[2090/(RT)]$, but there is limited significance.

Table II. Secondary Tritium Isotope Effects in Attack of *tert*-Butoxy Radicals on Xylenes

Xylene	a_t[a]	a_e[a]	$k_{CH_3}{}^H/k_{CH_2T}{}^H$
Para	3.47	2.11[b]	1.03
Para	3.47	2.08	1.00
Para	3.45	2.09	1.02
Meta	5.27	3.14	0.98
Meta	5.38	3.14	0.93

[a] Activities in 10^{-8} dpm/mol. [b] Determined from count of *p*-toluic acid instead of exchange sulfone.

The tritium isotope effects in Table I are virtually all intermolecular effects, and the deuterium isotope effects are pure intermolecular effects. The comparison of these results with some literature results which represent intramolecular isotope effects is facilitated by a knowledge of the magnitude of the secondary isotope effect. This was determined best in some studies on trace labeled xylenes. Of the active *m*- or *p*-methylbenzyl chlorides produced, the activity may be either in the methyl group ($TH_2CC_6H_4CH_2Cl$) or in the methylene group ($CH_3C_6H_4CHTCl$), and the relative amounts are determined by the rate constants $k_{CH_3}{}^H$ and $k_{CH_2T}{}^H$ in the radical-forming processes 4 and 5. The methylbenzyl chloride was converted to crystalline phenyl sulfone for determination of its specific molar activity, a_t, and the content of tritium in the methyl group was then determined by exchange in base by reaction 6, expressed as the specific molar activity after exchange, a_e. The secondary isotope effect is then given by eq 7 and the results of these experiments are presented in Table II. In one experiment, the *p*-methylbenzyl chloride was oxidized to *p*-toluic acid to give a_e, but since the yield was low, the method was inconvenient and possibly subject to error from isotope effects in the oxidation. Nevertheless, it shows that no gross error arises, for example, from incomplete exchange, in the ex-

$$Me_3CO\cdot + CH_3C_6H_4CH_2T \xrightarrow{3k_{CH_3}{}^H} Me_3COH + \cdot CH_2C_6H_4CH_2T \qquad (4)$$

$$Me_3CO\cdot + CH_3C_6H_4CH_2T \xrightarrow{2k_{CH_2T}{}^H} Me_3COH + CH_3C_6H_4CHT \qquad (5)$$

$$CH_3{*}C_6H_4CH_2{*}SO_2C_6H_5 + H_2O \xrightarrow[EtOH]{Et_3N} CH_3{*}C_6H_4CH_2SO_2C_6H_5 + H_2{*}O \qquad (6)$$

$$k_{CH_3}{}^H/k_{CH_2T}{}^H = 2a_e/3(a_t - a_e) \qquad (7)$$

Table III. Deuterium Isotope Effects for X· + $HCH_2Ph \rightarrow XH + \cdot CH_2Ph$

X·	t, °C	k_H/k_D[a]	% max[b]	ΔH_0[c]
t-BuO·	40	(5.4)[d]	77	−19
Ph·	60	4.2[e]	67	−27
CH_3·	115	(4–7)[f]	83–145	−19
Cl·	40	(2.5)[d]	36	−18
Cl·	40	1.8[d]	26	−18
Cl·	69.5	2.1[g]	35	−18
Cl·	77	1.3[h]	23	−18
Cl·	80	2.0[i]	36	−18
Br·	40	(6.2)[d]	86	−3
Br·	40	6.7[d]	96	−3
Br·	77	4.9[h]	89	−3

[a] Measured by various competitive methods. Parentheses show values calculated from k_H/k_T. [b] Calculated for total loss of zero-point energy, by $k_H/k_D = \exp(0.2107\nu_H/T)$, using $\nu_H = 2900$ for toluene. [c] Roughly estimated from bond dissociation energies. [d] This work. [e] R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963). [f] S. H. Wilen and E. L. Eliel, *ibid.*, **80**, 3309 (1958). [g] C. Walling and B. Miller, *ibid.*, **79**, 4181 (1957). [h] Reference 4. [i] H. C. Brown and G. A. Russell, *J. Am. Chem. Soc.*, **74**, 3945 (1952).

periments with sulfones. No isotope effects were detected in controls in the conversion of benzyl chlorides to the sulfones with sodium benzene sulfinate, but the difficulty of purifying the benzyl chlorides limits the precision of this statement to about ±2%. We may reasonably take the average of all the values in Table II and conclude that the secondary isotope effect is 0.99 ± 0.04. Secondary isotope effects were also measured by comparing the activity of other toluenes (a_T) with that of the substituted benzyl chlorides (a_b) produced at low conversion (counted as sulfones), using the equation $k_{CH_3}/k_{CH_2T} = 2a_b/3a_T$. Since at enough conversion to give a tractable yield there is some contribution of a primary isotope effect, this determination lacks precision, but results fell in the range $k_{CH_3}{}^H/k_{CH_2T}{}^H = 0.98 \pm 0.04$.

The possibility of a perceptible but small secondary isotope effect on chlorine atom reactions does exist. In the nearly thermoneutral bromination of $PhCH_2D$ and $PhCHD_2$, a small difference in the intramolecular k_H/k_D was attributed to a possible secondary effect amounting to less than 10% per D.[4] However, in the presumably more reagent-like chlorination the difference between the toluene-d_1 and toluene-d_2 results was less than experimental error. Similarly, in the nearly thermoneutral chlorination of methane, Persky[11] has reconciled several results with the assumption of a secondary isotope effect amounting at 40 °C to about 4% per deuterium.

It appears that we can safely neglect the secondary isotope effect in the *tert*-butyl hypochlorite reaction and probably also in the others. Although the large primary isotope effect suggests a "symmetrical" transition state, and a substantial secondary effect might therefore be expected, we should note that the two isotope effects are not necessarily measuring the same amount of product-like character, and need not therefore be correlated. We can therefore compare directly the intramolecular and intermolecular isotope effects, with only one reservation. If there are mechanistic complexities such that a step other than the actual hydrogen transfer is rate determining, then the two need not agree.

With the comparison now justified, Table III presents a few of the results in Table I, together with some literature results, which emphasize the variability of these isotope effects.

In this table we express in the fourth column the isotope effect as fraction of the "maximum", mainly because this form removes much of the temperature sensitivity, and allows comparison between results at somewhat different temperatures. Now it can be seen that the *tert*-butoxy radical results are fairly comparable to those with methyl and phenyl radicals at more than 60% of "maximum" but that the chlorine atom results are all less than 40% of "maximum". Clearly the value of ΔH_0, even though very rough, is not useful in predicting the isotope effect, for the smallest isotope effect is associated with the chlorine atom, which forms about as strong a new bond as CH_3· or $(CH_3)_3CO$· and weaker than Ph·.

We suggest that ΔH alone is an insufficient measure of transition state asymmetry. Not only must a reaction be highly exothermic to have a very reagent-like transition state, but the exothermicity must be large compared to the activation energy. It is in this respect that chlorine atoms occupy a special position; not only is the reaction with toluene exothermic by about 18 kcal, but the activation energy is smaller than any of the other highly exothermic cases. For Cl· reacting with toluene the activation energy must be very small, probably less than 2 kcal, for even for the reaction with methane, E_a is only about 4 kcal. However, the t-BuO· attack on toluene has $E_a = 5.6 \pm 2$ kcal[12] or 4.3 kcal and for methyl attack E_a is about 7.4 kcal. Data for phenyl attack are not available. We suggest as a first guess that activation energies for exothermic reactions will be large if both atoms flanking the hydrogen in the transition state are in the first row, but will be much smaller if either the hydrogen atom donor or acceptor is in the second row or later. We can further expect a large change in isotope effect when one element is not in the second row, but when both elements are in the first row, we can expect large isotope effects with minor variations with substantial changes in ΔH. The following additional observations confirm this view.

1. The isotope effects in hydrogen transfer from sulfur to carbon cover a wide range.[1-3]

2. Isotope effects in bromine atom attack on toluene cover a wide range, from 90% of maximum with toluene itself to 47% of "maximum" with ethylbenzene and only 31% with cumene.[4]

3. Isotope effects in reaction of radicals with HBr covered a range of a factor of 4; the "maximum" used in the other cases is not useful here.[13]

4. Not only do hydrogen atom abstractions from carbon to oxygen give large isotope effects, but in the attack of poly(vinyl acetate) radicals on phenols, the isotope effect is large and varies over a rather small range.[14]

5. The greater activation energy of *tert*-butoxy radicals and methyl radicals relative to chlorine atoms is also reflected in the greater selectivity of the oxygen and carbon radicals, for example, in their reactions with ethylbenzene. An alternative suggestion of the high selectivity of *tert*-butoxy radicals was that the forming OH bond was unexpectedly weak.[15] This appears to be a less attractive explanation.

The use of position in the periodic table appears to be useful to qualitatively predict activation energies and hence isotope effects. However, clearly it is only a first approximation, and more sophisticated approaches can do better. So far the only conspicuous failures in relating isotope effect to position in the periodic table are the large and apparently random isotope effects in the addition of dimethyl phosphonate and dimethyl thionephosphonate to olefins,[16] and steric effects are probably very large.

The following conclusions may now be drawn. 1. For a thermoneutral hydrogen atom transfer the isotope effect will be not less than the maximum value calculated for complete loss of the stretching vibration zero-point energy of the breaking bond. Larger values may arise from tunnel corrections.

2. For exothermic hydrogen transfer reactions the isotope effect will fall from the tunnel corrected "maximum" value to a lesser value, decreasing with exothermicity.

3. The fall off of the isotope effect as ΔH becomes more negative will be modified by two effects. (a) Pronounced steric hindrance in the transition state will increase the isotope effect (both classically and with tunnel correction). (b) Contributions of special transition state structures such as polar contributions will decrease the isotope effect. Alternatively, an exothermic reaction will appear more symmetrical, that is, less reagent-like, with steric hindrance, and less symmetrical with important polar contributions. Endothermic can probably be substituted everywhere for exothermic, although the data are sparse.

4. The extent to which the isotope effect falls of with increasing exothermicity depends on the ratio of $E_a/\Delta H$. When this ratio is nearly zero, very unsymmetrical transition states can be achieved, and the Westheimer symmetry effect[17] is important. When E_a is larger relative to (ΔH), all transition states are very nearly "symmetrical",[18] and closely resemble the proton transfer isotope effects, where much of the isotope effect variation appears to result from variation in the tunnel correction.[19-21] Relatively low E_a appears to be associated with transfer to or from 2d row or later row elements. Two first-row elements appear to lead to higher isotope effects.

Experimental Section

Materials. *tert*-Butyl hypochlorite was made and assayed by literature methods.[22]

The variously substituted tritium-labeled toluenes were made from the corresponding substituted benzyl chloride (distilled from commercial materials) via treatment of the Grignard reagent with tritiated water. The following synthesis of *p*-xylene is typical. Magnesium turnings (12.2 g, 0.5 mol) were placed in a flask with 150 ml of ether and stirred with a slow sweep of nitrogen gas. α-Chloro-*p*-xylene (70.5 g, 0.5 mol) and 100 ml of ether were placed in a dropping funnel over the flask, a small amount of iodine was added to the magnesium and ether, and the solution of the chloride was added dropwise over a period of 2 h. The solution became dark green in color. Tritium-labeled water (about 0.4 ml, ca. 0.4 mCi) was added, then after 30 min an excess of ordinary water containing an excess of ammonium chloride. The ether phase was separated, dried over magnesium sulfate, and distilled, yielding 40 g (0.38 mol, 75%) of *p*-xylene, bp 138–139 °C. This, like the other toluenes, had about 4×10^8 dpm/mol, giving about 17% incorporation of tritium from water. The low value presumably is due to occlusion of water in the first precipitate.

Sodium benzenesulfinate was a commercial material used to convert the benzilic chloride to sulfones. The following preparation of *p*-methylbenzyl phenyl sulfone is typical. *p*-Methylbenzyl chloride, 0.154 g (1.1 mmol), sodium benzenesulfinate dihydrate (0.4711 g, 3.2 mmol), and ethanol (15 ml) were heated together under reflux for 4 h. The reaction mixture was poured into ice-water, and the precipitated product was recrystallized from ethanol: yield 0.237 g; 88%; mp 153–154 °C. Other benzyl phenyl sulfone yields and melting points were, in that order: *m*-CH_3, 50%, 124–125 °C; unsubstituted, 92%, 149–150 °C.

Exchange of Tolyl Phenyl Sulfones. The tritium was removed from the *m*- and *p*-methylbenzyl phenyl sulfones by boiling the sulfone (ca. 0.29) with ethanol (5 ml), water (0.5 ml), and triethylamine (1 ml) for 20 h. The sulfone was recovered by diluting with cold water, and it was recrystallized from ethanol.

Degradation of *p*-Methylbenzyl Chloride. *p*-Methylbenzyl chloride (0.3 g), dimethyl sulfoxide (0.5 g), and acetic anhydride (5 ml) were heated together on the steam bath for 22 h. The solution was poured into ice–water and extracted with ether; the ether layer (50 ml) was washed with dilute hydrochloric acid and oxidized further with 5% hydrogen peroxide (20 ml) by stirring at room temperature for 5 h. Conventional work-up yielded *p*-toluic acid (0.03 g), mp 181–181.5 °C, from benzene–hexane.

Isotope Effect in *tert*-Butyl Hypochlorite Chlorination. The following is a typical run on toluene. Toluene (2.32×10^8 dpm/mol, 3.139 g) was dissolved in 25 ml of Freon 113, 1,1,2-trichloro-1,2,2-trifluoroethane, which was 0.8 N in *tert*-butyl hypochlorite, 4.09 g of chlorobenzene (as internal standard for GC), and 0.73 g of trichloroethylene and diluted to 50 ml with further Freon 113. Of this 40 ml was placed in a Pyrex ampoule, degassed, and sealed under vacuum. It was then placed in the thermostat at 40 °C and exposed to a sunlamp for 20 min. Water (10 ml) was then added to the ampoule on opening, and the water phase was twice washed with pentane and then counted. The organic layer was washed twice with 50% sodium thiosulfate solution, dried over magnesium sulfate, and subjected to GC analysis, which showed that 89.1% of the toluene remained unreacted, and the yield of *t*-BuOH is 10.9%. The isotope effect is given by the expression $k_H/k_T = 3a_{Me_3COH}/a_{PhCH_3}$. The factor of 3 is statistical; with xylenes the factor is 6.

The activity of *t*-BuOH is given by the expression $a_{t\text{-BuOH}} =$ (specific activity of water)(fraction of whole water sample counted)/0.109. This method reduces errors due to exchange of tritium with vessel walls; it does not require quantitative extraction of the alcohol, since it is exchanged, and a second extraction of the organic layer found substantially less than 1% of the activity of the first. The pentane extractions remove traces of the much more active toluene from the water extract, and again a slight loss of alcohol no longer matters.

Isotope Effect in Chlorination. A somewhat different experimental technique was required. The reaction was contained in a cylindrical Pyrex reaction vessel in a thermostat at 40 °C through which a mixture of nitrogen and chlorine gas could be passed. The gas then passed through a reflux condensor and then through two bubblers: the first containing 25 ml of 2% potassium hydroxide, the second 10 ml of 2% potassium hydroxide. The toluene, (0.3 g) together with a nearly equivalent amount of chlorobenzene as a GC internal standard, was dissolved in Freon 113 to make 50 ml. A sunlamp close to the reaction vessel was turned on, the chlorine and nitrogen flows were started, and reaction continued for a time (dependent on flow rates, and on the light source and location) sufficient to consume between 10 and 30% of the toluene. Then the contents of the two bubblers were added to the reaction vessel, and the two-phase system was treated as in the hypochlorite ester reactions.

The bromination isotope effect was measured as in the chlorine case, except that bromine was introduced by passing the nitrogen stream through liquid bromine. There was always an excess of bromine in the reaction vessel, apparently enough to prevent reaction of benzyl radicals with HBr.

Isotope Effects with Toluene-d_3. The conditions were the same as for the tritium isotope effects except that an equal mixture of toluene and toluene-d_3 (commercial, 99.5% deuterated) was used and no chlorobenzene was used. After halogenation, the reaction mixture was washed with cold sodium sulfite solution, dried, and distilled. The benzyl chloride fraction was converted with sodium *p*-toluenesulfinate to a sulfone and recrystallized (mp 127–128 °C) following the methods developed for the phenyl sulfones above. The deuterium content then was determined by the ratio of methyl to methylene peak areas in the NMR. The extents of completion were for *t*-BuOCl, 3%, for Cl_2, 14.3%, and for Br_2, 9.1%; because of the rather large isotope effect the last contains a perceptible error in the use of the linear approximation, giving rise to an isotope effect somewhat too low. The estimated error in the table includes this factor.

Acknowledgment. We thank the Robert A. Welch Foundation for a grant which supported this work.

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Isotope Effects in Hydrogen Atom Transfers. VIII. Addition of Dimethyl Phosphonate and Thiophosphonate to Olefins[1]

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Received June 26, 1975

Abstract: The free-radical chain addition of dimethyl phosphonate and dimethyl thiophosphonate to olefins has as a step the reaction $R_2\dot{C}CH_2PX(OCH_3)_2 + HPX(OCH_3)_2 \rightarrow R_2CHCH_2PX(OCH_3)_2 + \cdot PX(OCH_3)_2$ (X = O or S). In some cases this reaction does not compete with polymerization, in others fairly good yields of 1:1 adducts are isolable; telomers also result. It is therefore suspected that the reaction is not far from thermoneutral. Tritium isotope effects are often larger than that calculated for complete loss of P–H stretching vibration, and show no obvious structural correlation. The isotope effect is therefore not useful in ordering bond energies. It is believed that there is a large steric enhancement of the isotope effect, and that tunnel corrections are substantial.

Dimethyl phosphonate, $HPO(OCH_3)_2$, and dimethyl thiophosphonate, $HPS(OCH_3)_2$, add to some olefins with the chain-carrying steps 1 and 2.[2]

$$R_2C{=}CH_2 + \cdot PX(OCH_3)_2 \rightarrow R_2\dot{C}\text{-}CH_2PX(OCH_3)_2 \quad (1)$$

$$R_2\dot{C}\text{-}CH_2PX(OCH_3)_2 + HPX(OCH_3)_2 \rightarrow R_2CHCH_2PX(OCH_3)_2 + \cdot PX(OCH_3)_2 \quad (2)$$

$$(X = O \text{ or } S)$$

The isotope effect in hydrogen-atom transfer reactions has been shown to be sensitive to a number of factors, notably the bond-dissociation-energy difference, or ΔH,[3,4] steric influences,[5] contributions of polar structures to the transition state,[6] as well as the position in the periodic table of the atoms between which the hydrogen is being transferred.[7] It has not been necessary to call upon variation due to nonlinearity of the transition state, nor have bending vibrations been shown to be important in polyatomic cases.[8] Although good values of ΔH for the H atom transfer, eq 2, are not available, it can be concluded that ΔH is fairly close to zero, for although the addition of 1-alkenes to dimethyl phosphonate is quite practical, styrene does not add, instead it polymerizes, suggesting (although not proving) that the radical from styrene is too stable to attack the HP bond. Styrene does add to dimethyl thiophosphonate, suggesting a slightly weaker PH bond in this compound. No bond dissociation energies for these PH bonds are available; the above argument underestimates the exothermicity unless these PH bonds are stronger than that in phosphine, with D_{PH} = 77 kcal.[9]

It is convenient to compare observed isotope effects with the so-called "maximum", calculated for complete loss of the stretching vibration zero-point energy of the breaking bond, with no effect of other vibrations and no tunnel correction. The "maximum" isotope effect is given by $(k_H/k_D)_{max} = \exp[h(\nu_H - \nu_D)/2kT]$, where $h\nu_H/2$ is the stretching zero-point energy of the bond to hydrogen in the reagent. Assuming harmonicity, and large masses of other atoms, this becomes numerically $(k_H/k_D)_{max} = \exp(0.21071\nu_H/T)$, where ν_H is in cm^{-1}. Correspondingly $(k_H/k_T)_{max} = \exp(0.30405\nu_H/T)$. These "maximum" effects refer only to those imposed by the one-dimensional three-particle model without tunnelling. The frequencies taken were those measured in dilute solution in carbon tetrachloride, that is 2444 cm^{-1} for $HPO(OCH_3)_2$ and 2416 cm^{-1} for $HPS(OCH_3)_2$.[10] These lead to "maximum" k_H/k_T of 7.7 for X = O at 90 °C and 8.0 for X = S at 80 °C. Our results are presented in Table I at 90 °C for the oxygen ester and at 80 °C for the sulfur ester. Many entries in Table I have isotope effects greater than the "maximum". It is probably possible to rationalize the isotope effects in the table by combinations of bond dissociation energy effects, deformed by various neighboring group effects and modified by other effects. However, there are not enough data to make such a rationalization convincing, and we prefer to note only that ΔH is not far from zero, making the transition nearly symmetrical and the isotope effects generally large, that phosphorus is in the second row, so that the isotope effect can be expected to drop off significantly for ΔH well removed from zero, and that the transition state (I) is very likely sterically hindered, giving the isotope effect the opportunity, through tunnelling, to substantially exceed the maximum.

Another presentation which shows the anomalies of the substituent effect in a different way is illustrated in Figure