value for the same experiment and smaller at two temperatures than our values obtained from the tritium values. The discrepancy is disturbing, but is not large enough to change our arguments.

- (6) C. G. Swain, E. C. Stivers, J. F. Reuwer, and L. J. Schaad, J. Am. Chem. Soc., 80, 5585 (1958).
- H. Sakurai and A. Hosomi, J. Am. Chem. Soc., 89, 458 (1967).
 A. A. Zavitsas and A. A. Melikian, J. Am. Chem. Soc., 87, 2757 (1975).
 A. A. Zavitsas and J. D. Blanks, J. Am. Chem. Soc., 94, 4603 (1972).
- (10) P. Wagner and C. Walling, J. Am. Chem. Sci., 87, 5179 (1965).
 (11) A. Persky, J. Chem. Phys., 60, 49 (1974).
- (12) D. J. Carlsson, J. A. Howard, and K. U. Ingold, J. Am. Chem. Soc., 88, 4725 (1966).
- (13) E. S. Lewis and S. Kozuka, J. Am. Chem. Soc., 95, 282 (1973). (14) M. Simonyi, I. Fitos, J. Kardos, I. Lukovits, and J. Pospisil, J. Chem. Soc., Chem. Commun., 252 (1975).
- (15) I. K. Stoddert, A. Nechvatal, and J. M. Fedder, J. Chem. Soc., Perkin *Trans. 2, 4*73 (1974). (16) E. C.-Y. Nieh, Ph.D. Thesis, Rice University, 1972.
- (17) F. H. Westheimer, Chem. Rev., 61, 265 (1961).
- (18) "Symmetrical" is used in the rather artificial sense of a transition state containing very little isotopic mass sensitive zero-point energy in the one-dimensional three-particle approximation. The interpretation in terms of a quadratic approximation of the energy surface is presented by E. S. Lewis, "Isotopes in Organic Chemistry", Vol. II, E. Buncel and
- C. C. Lee, Ed., Elsevier, in press.
 R. P. Bell, W. H. Sachs, and R. L. Tranter, *Trans. Faraday Soc.*, 67, 1995 (1971).
- (20) J. R. Keefe and N. H. Munderloh, J. Chem. Soc., Chem. Commun., 17 (1974).
- (21) E. C. Caldin, Chem. Rev., 69, 135 (1969).

Isotope Effects in Hydrogen Atom Transfers. VIII. Addition of Dimethyl Phosphonate and Thiophosphonate to Olefins¹

E. S. Lewis* and E. C. Nieh

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. Received June 26, 1975

Abstract: The free-radical chain addition of dimethyl phosphonate and dimethyl thiophosphonate to olefins has as a step the reaction $R_2CCH_2PX(OCH_3)_2 + HPX(OCH_3)_2 \rightarrow R_2CHCH_2PX(OCH_3)_2 + PX(OCH_3)_2$ (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(OCH₃)₂, add to some olefins with the chain-carrying steps 1 and 2.2

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

$$R_{2}\dot{C}-CH_{2}PX(OCH_{3})_{2} + HPX(OCH_{3})_{2} \rightarrow R_{2}CHCH_{2}PX(OCH_{3})_{2} + \cdot PX(OCH_{3})_{2} \quad (2)$$

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

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 $(k_{\rm H}/$ $k_{\rm D})_{\rm max} = \exp[h(\nu_{\rm H} - \nu_{\rm D})/2kT]$, where $h\nu_{\rm H}/2$ 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 $(k_{\rm H}/k_{\rm D})_{\rm max}$ $\exp(0.21071\nu_{\rm H}/T)$, where $\nu_{\rm H}$ is in cm⁻¹. Correspondingly $(k_{\rm H}/k_{\rm T})_{\rm max} = \exp(0.30405\nu_{\rm H}/T)$. 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(OCH₃)₂ and 2416 cm^{-1} for HPS(OCH₃)₂.¹⁰ These lead to "maximum" $k_{\rm H}/k_{\rm T}$ 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

Table I. Tritium Isotope Effects and Yields in the Addition ofDimethyl Phosphonate and Dimethyl Thiophosphonateto Unsaturated Compounds

	$HP(O)(OCH_3)_2^a$		$HP(S)(OCH_3)_2^b$	
Unsaturated compd	$k_{\rm H}/k_{\rm T}^c$	Yield, ^d %	$k_{\rm H}/k_{\rm T}c$	Yield,d %
PhCH==CH,		е	3.8	30
AcOCH,CH=CH,	4.9	>80	5.6	>80
CH ₃ OC(O)CH=CH ₂		е	6.7	47
$AcOCH_2(CH_3)C = CH_2$	6 .0	>80	7.6	>80
C ₂ H ₅ OCH=CH ₂	6.1	40	8.7	>80
$AcO(CH_3)C = CH_2$	10.0	78	7.2	>80
AcOCH=CH ₂	12.4	27	8.1	37
(CH ₃) ₃ SiCH ₂ CH=CH ₂	11.1	>80	9.6	>80
PhOCH ₂ CH=CH ₂		f	8.4	>80
NCCH ₂ CH=CH ₂		f	8.3	>80
PhCH ₂ CH=CH ₂	11.9	>80	8.1	> 80
$PhCH_2(CH_3)C = CH_2$	10.0	> 80	7.0	>80
$n-C_6H_{13}CH==CH_2$	8.7	>80	6.8	>80
CH ₂ (CH ₂) ₅ CH=CH	8.4	>80	7.3	>80
CH ₂ (CH ₂) ₃ CH=CH	9.1	>80		d
CH ₂ (CH ₂) ₂ CH=CH	7.5	>80		d
PhC==CH		f	6.5	43
n-C₄H₅C==CH	6.4	528,h		i
(CH ₃) ₃ CCH=CH ₂	6.1	60 ^h	6.4	53

^{*a*} Reactions were carried out at 90 ± 0.1 °C with benzoyl peroxide as catalyst. ^{*b*} Reactions were carried out at 80 ± 0.1 °C with AIBN as catalyst. ^{*c*} All isotope effects calculated from the linear approximation, introducing a systematic error of underestimating the isotope effect by less than 5%. ^{*d*} The balance of material was primarily in the form of telomer unless otherwise noted. ^{*e*} Failed to isolate any 1:1 adduct due to extensive polymerization of olefin. ^{*f*} Not tried. ^{*g*} The balance of material was in the form of unreacted olefin. ^{*i*} No 1:1 adduct isolated. Major product is the saturated bisphosphonic ester.



1, a plot of the isotope effect with dimethyl phosphonate vs. that with dimethyl thiophosphonate. The two "maximum" isotope effects are shown as dashed lines. Figure 2 is the same type of plot when the two reagents are thiophenol and α -toluenethiol, with a series of radicals.⁵ Figure 3 shows a hypothetical plot of isotope effect vs. bond-dissociation energy of the forming bond, $D_{\rm RH}$, for a series of atom transfers from ZH to YH to R. The curves are arbitrarily chosen as Gaussian curves (+1) with maxima at $D_{\rm RH} = D_{\rm ZH}$ and $D_{\rm RH} = D_{\rm YH}$, respectively. The isotope effects (i.e.)_Z and (i.e.)_Y are given by the equation (i.e.)_Z = 1 + $6e^{-x^2}$, (i.e.)_Y = 1 + $6e^{-(x-x_1)^2}$; the number 6 is chosen only to give a familiar maximum effect of 7. The use of any other function with a maximum is equally defensible. This leads to a family of curves such as Figure 4, in which the isotope effect with ZH is plotted against that with YH. The curve resembles a baseball bat when D_{ZH} is quite close to D_{YH} (compared to the width of the curves), that is, for small x_1 ; when the difference between D_{ZH} and D_{YH} (or x_1) increases, the curve becomes fatter and finally separates into two lobes. The general shape of these plots is not sensitive to the form of the curve of Figure 3, so long as it has a maximum and falls to unity on both sides reasonably symmetrically and smoothly.



Figure 1. Plot of tritium isotope effect for addition to dimethyl thiophosphonate vs. that for addition to dimethyl phosphonate. Each point corresponds to a particular olefin. The dotted lines are the "theoretical maximum" isotope effect for each reagent at the experimental temperature.



Figure 2. Plot of tritium isotope effect in the addition of thiophenol to olefins vs. that for addition of α -toluenethiol to the same olefin. The curve is similar to those in Figure 4, except that the two maxima are slightly different and $x_1 = 0.3$



Figure 3. A hypothetical plot showing the symmetry effect on the isotope for radical abstraction from two different thiols. The maxima correspond to the points where $D_{CH} = D_{SH}$, different for the two thiols. The curves are Gaussian, of the form i.e. = $1 + 6e^{-x^2}$ and $1 + 6e^{-(x-x_1)^2}$, respectively.

The reasonable conformity of Figure 2 to an intermediate member of the family of Figure 4 suggests that curves like those of Figure 3 apply roughly to both isotope effects. The curve drawn in Figure 2 uses a maximum of 10 on one axis

Lewis, Nieh / Addition of Dimethyl Phosphonate and Thiophosphonate to Olefins



Figure 4. A plot of one isotope effect against another from curves such as those of Figure 3. Each curve is for a different separation (x_1) of the two maxima.

and 12 on the other; the value $x_1 = 0.3$ is a better fit than $x_1 = 0.2$ or 0.4, but is otherwise not justified. The "maximum" tritium isotope effect calculated for an average 2575-cm⁻¹ SH bond at 70 °C is 9.8, which with a normal symmetry-dependent tunnel correction could become as high as the values chosen. Most of the points in Figure 2 fall below this "maximum" value. The quality of fit to eq 2 is unimpressive. However, evidence has been presented^{3,4,5} that the transfers from thiols do indeed show principally bond-energy influence on the isotope effects, and the roughness of the fit indicates that some other factors also contribute to a lesser extent. We use this rough fit as alternative evidence that in this case the bond energies are the predominant factor in determining the isotope effects. The scatter of Figure 1 suggests that at least one and probably both isotope effects are not correlated with $D_{\rm RH}$ of the forming bond. The dotted lines in Figure 1 show the "maximum' and only three points fall within the maximum limits for both X = O and S. We suggest that the unusually large isotope effects are associated with the failure to correlate with bond energies, and that the failure is attributable to steric enhancement of both the classical isotope effect and of the tunnel correction. This steric enhancement of the isotope effect is likely to broaden out the maximum in a curve such as Figure 3 as well as markedly increasing the tunnel correction.⁸ Since the steric hindrance in the transition state does not correlate with bond energy of the forming bond, it will produce a random increase in the isotope effects over those of curves like Figure 4. A referee suggested that reversal of reaction 2 may invalidate the calculation of the isotope effect. Indeed it would, but it would make the calculated isotope effect closer to the small equilibrium isotope effect, and if this reversal were to contribute, the true kinetic isotope effects would be even larger than those in the table and therefore even less susceptible to simple explanation. There is, however, no evidence for reversal.

Experimental Section

Materials. Olefins and other reagents not specifically mentioned were commercial materials.

Dimethyl Phosphonate-t. Dimethyl phosphonate (commercial) (440 g, 4 mol) was mixed with 2 ml of tritiated water ($\sim 1 \text{ mCi/g}$) and a few drops of acetic acid. After 24 h, the mixture was dried over Drierite, and then fractionally distilled to yield a center fraction, 395 g, bp 64-65 °C (15 mm). This fraction was redistilled to constant specific activity. It showed no detectable water content by NMR when freshly distilled, but was significantly hygroscopic in air.

Dimethyl Thiophosphonate. Dimethyl chlorophosphinate was

prepared by redistribution of commercially available trimethyl phosphite and phosphorus trichloride, then this was treated with hydrogen sulfide.¹¹ Trimethyl phosphite (248 g, 2 mol) was added slowly to phosphorus trichloride (173 g, 1 mol) over a period of 1 h with stirring, during which time the temperature rose to about 45 °C. The solution was held at about this temperature for another hour, and then distilled through a short Vigreux column, yielding a fraction (238 g, bp 32-40 °C (40 mm)) composed of a mixture of dimethyl chlorophosphinate and methyl dichlorophosphinate in about a 3:1 ratio. Several such fractions were combined for a second distillation through a 14 in. glass helix packed column, giving dimethyl chlorophosphinate (bp 32-34 °C (40 mm)) characterized by the proton spectrum at δ 3.57 ppm with $J_{PH} = 11$ Hz.

Dimethyl chlorophosphinate (46 g, 0.3 mol) was mixed with trimethylamine (33 g, 0.3 mol) in 1 l. of anhydrous ether and cooled to -10 to -15 °C. Hydrogen sulfide was passed in with vigorous stirring until it was no longer absorbed. The mixture was then filtered, the filtrate washed with water, dried over Drierite, concentrated on the rotary evaporator, and distilled, yielding 28 g (74%) of dimethyl thiophosphonate (bp 52-54 °C (12 mm)) in agreement with the literature,¹² with proton NMR at δ 3.82 (6 H, d, J_{PH} = 14 Hz) and 7.76 (1 H, d, $J_{PH} = 664$ Hz). Caution: Attempts at scaling this preparation up led to serious overheating with uncontrollable loss of malodorous material. The procedure for exchange with tritiated water followed exactly that for the oxygen analogue.

Addition of Dimethyl Phosphonate to Olefins. The olefin (0.03 mol), dimethyl phosphonate-t (0.4 mol), and benzoyl peroxide (0.0015 mol) were placed in a glass ampoule. The contents were then degassed, and the ampoule was sealed. The ampoule was then plunged into a thermostated oil bath at 90 \pm 0.1 °C for 8 h. Then the ampoule was cooled, opened, and the contents distilled under vacuum. Distillation was repeated to isolate the 1:1 adduct, characterized by proton NMR, infrared, and occasionally the mass spectrum. The adduct was counted and in most cases redistilled to constant specific activity. The yields were quite structure dependent and are presented in the table.

Addition of Dimethyl Thiophosphonate to Olefins. The procedure followed that for dimethyl phosphonate with three exceptions: (1) the amount of ester was 0.2 mol; (2) the initiator was azobisisobutyronitrile; (3) the temperature was 80 ± 1 °C.

Isotope Effects. Isotope effects were calculated using the linear approximation,¹³ i.e., $k_{\rm H}/k_{\rm T} = a_{\rm (MeO)_2PXH}/a_{\rm adduct}$, which is adequately accurate since there was never less than a ten-fold excess of the tritiated ester reagent. Furthermore, the major side reaction is telomer formation; thus more than 1 mol of the olefin was used per mole of phosphonate, so the real excesses were even greater. Corrections for the finite excess thus are not possible, but the errors introduced are less than 5%. Counting was done by solution scintillation counting with recently calibrated automatic external standardization. The major error appears to lie in the hygroscopic character of dimethyl phosphonate. To the extent that a counted sample is wet, and exchanged, tritium is partitioned between the ester and the water, and that in water is unavailable for the freeradical chain, since the exchange is probably slower than the olefin addition.¹⁴ Hence, contaminating water will make the measured specific molar activity of dimethyl phosphonate high, and the isotope effect also high. The major effort to overcome this problem was to distill the ester just before use, and to redistill frequently to constant activity. A 1% by weight water contamination could cause about a 12% error in the isotope effect, because of the equivalent weight difference. We believe that the levels were well below this, but there may be an error of not more than about 5% in the isotope effect from this source. Results of duplicate experiments are not shown, but isotope effects fell within 3% of the mean shown.

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

References and Notes

- From the Ph.D. Thesis of E. C. Nieh, Rice University, 1972.
- C. Walling and M. S. Pearson, *Top. Phosphorus Chem.*, 3, 1 (1963).
 E. S. Lewis and M. M. Butler, *Chem. Commun.*, 941 (1971).
- W. A. Pryor and K. G. Kneipp, J. Am. Chem. Soc., 93, 5584 (1971).
- (5) E. S. Lewis and M. M. Butler, J. Am. Chem. Soc., accompanying paper in this issue: part V.
- (6) E. S. Lewis and K. Ogino, J. Am. Chem. Soc., accompanying paper in

- (7) E. S. Lewis and K. Ogino, J. Am. Chem. Soc., accompanying paper in this issue: part VII.
- E. S. Lewis, "Isotopes in Organic Chemistry", Vol. II, E. Buncel and C.
- C. Lee, Ed., Elsevier, Amsterdam, in press.
 W. G. Bentrude, "Free Radicals," J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 22.
- (10) R. Wolf, D. Honalla, and F. Mathis, Spectrochim. Acta, Part A, 23, 1641 (1960); J. G. David and H. E. Hallam, J. Chem. Soc. A, 1103 (1966).
- (11) A. C. Still, U. S. Patent 2,895,982 (1939); H. C. Cook, J. D. Itett, B. C. Saunders, G. J. Stacey, H. G. Watson, I. G. Wilding, and S. J. Woo-docks, J. Chem. Soc., 2921 (1945).
 (12) R. Saliman, German Patent 1,036,251 (1958); Chem. Zentralbi., 4289
- (1959). (13) L. Melander, "Isotope Effects on Reaction Rates", Ronald Press, New
- York, N.Y., 1960, p 58. (14) Z. Luz and B. Silver, J. Am. Chem. Soc., 84, 1095 (1962); P. R. Ham-mond, J. Chem. Soc., 1365 (1962).

Nucleophilic Substitution Reactions in Fluorinated Bis(arene)chromium Complexes¹

Michael J. McGlinchey* and Teong-Seng Tan

Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada. Received May 16, 1975

Abstract: Fluorinated bis(arene)chromium complexes undergo nucleophilic substitution reactions, with loss of fluoride. under very mild conditions in an analogous fashion to hexafluorobenzene. Thus, $bis(\eta$ -fluorobenzene) chromium reacts with sodium methoxide to yield $bis(\eta$ -methoxybenzene)chromium. (η -Benzene)(η -hexafluorobenzene)chromium (2) reacts with alkyl or aryl lithium reagents at -78° to give polysubstituted products. Furthermore, tert-butyllithium abstracts a proton from the π -complexed C₆H₆ ring in 2 to generate a new nucleophile which attacks 2 to yield 6, which has a bridging pentafluorobiphenyl group.

The chemistry of bis(arene)chromium complexes has hitherto been restricted to metalation reactions²⁻⁴ and basecatalyzed hydrogen-deuterium exchange processes.^{5,6} Electrophilic or free radical attack on the complexed arene rings is unlikely owing to the presence of the relatively electronrich chromium atom which provides a much more attractive target for an incoming electrophile. Conversely, nucleophilic attack on the complexed rings should be enhanced relative to the free arene, and indeed in the corresponding arene-chromium tricarbonyl systems synthetic schemes have been based on this premise.⁷

However, nucleophilic displacement requires the presence of a suitable leaving group, and such systems cannot be synthesized by the route pioneered by Fischer and Hafner,⁸ since arenes possessing substituents with nonbonded electron pairs react with the Lewis acid catalyst (AlCl₃) thus preventing formation of sandwich complexes. Fortunately the recently developed metal atom cocondensation technique^{9,10} provides a viable synthetic route by which leaving groups (e.g., halogens) can be incorporated into chromium-arene sandwich compounds.11-14

Results and Discussion

¹⁹F NMR studies on a series of fluoro-substituted bis(arene)chromium complexes indicated that a π -complexed chromium atom has a similar effect on an aromatic ring as do four ring fluorine atoms.¹³ Thus, $bis(\eta-1,4-difluoroben$ zene)chromium would be expected to undergo nucleophilic substitution with loss of fluoride ion in an analogous fashion to the known chemistry of hexafluorobenzene.¹⁵ Preliminary experiments with $bis(\eta$ -fluorobenzene)chromium and sodium methoxide led to a very low yield of $bis(\eta$ -methoxybenzene) chromium (1), which was identified by comparison



of its mass spectrum and proton NMR spectrum with that of an authentic sample made by the direct reaction of anisole with chromium atoms. However, the reported synthesis by Timms¹² of $(\eta$ -benzene) $(\eta$ -hexafluorobenzene)chromium (2) by the cocondensation procedure provided an ideal system in which nucleophilic substitution could occur in only one ring. Hexafluorobenzene complexes of other metals have been reported, but they are of low thermal stability.¹⁶ Although hexafluorobenzene reacts with sodium methoxide or piperidine at moderate temperatures,¹⁵ no appreciable reaction with 2 was observed even after several hours reflux at 60°. Butyllithium is reported to react with C_6F_6 at -78° to produce a mixture of mono-, di-, tri-, and tetrasubstituted products, whereas tert-butyllithium yields only the mono- and disubstituted arenes.17

Accordingly, a 5 molar excess of n-butyllithium and 2 were mixed in ether at -78° and upon warm-up the major product isolated was the tetrasubstituted derivative 3. The



product was identified by its mass spectrum (see Table I) which showed the parent ion and loss of fluorines and alkyl groups. The major fragmentation route in this case, as with many others we have studied, involves cleavage of the fluoroarene-chromium bond with loss of C_6H_6 -Cr (m/e 130) and subsequent breakdown of the substituted ring. The ¹⁹F NMR of 3 in deuteriobenzene shows a single peak at 180.2 ppm to high field of CFCl₃, suggesting the para isomer; this assignment is reinforced by the observation that the spectrum 24 h later (the solution having changed from red to green due to decomposition of the complex) showed a peak at 126.7 ppm, while the free arene, 1,2,4,5-tetrakis(nbutyl)-3,6-difluorobenzene, is reported to absorb at 127.2

McGlinchey, Tan / Fluorinated Bis(arene)chromium Complexes