(6) (a) J. L. Lyle and R. W. Taft, *J. Heterocycl. Chem.*, **9**, 745 (1972); (b) P. B. Desai, *J. Chem. Soc., Perkin Trans. 1*, 1865 (1973); (c) M. M. Boudakian, U.S. Patent 3,703,521, Nov 1972.
(7) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley, New York, N.Y., 1972, p 23.
(8) (a) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 11 (1970), and references therein; (b) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960 (1968).
(9) S. D. Sharma and S. Doraiswamy, *Curr. Sci.*, **41**, 475 (1970).
(10) B. Bak, L. H. Nygaard, and J. R. Anderson, *J. Mol. Spectrosc.*, **2**, 361 (1958).
(11) P. C. Rerat, *Acta Crystallogr*, **15**, 427 (1962).
(12) A. J. Jones, D. M. Grant, J. G. Russell, and G. Fraenkel, *J. Phys. Chem.*, **73**, 1624 (1969).
(13) (a) T. F. Page, Jr., *Mol. Phys.*, **13**, 523 (1967); (b) A. R. Tarpley, Jr., and J. H. Goldstein, *J. Phys. Chem.*, **76**, 515 (1972).
(14) F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **93**, 2361 (1971).
(15) R. J. Pugmire and D. M. Grant, *J. Am. Chem. Soc.*, **90**, 697 (1968).
(16) W. M. Litchman and D. M. Grant, *J. Am. Chem. Soc.*, **90**, 1400 (1968).
(17) (a) N. Muller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963); (b) D. Doddrell, D. Jordan, N. V. Riggs, and P. R. Wells, *J. Chem. Soc., Chem Commun.*, 1158 (1972).
(18) M. Hansen and H. J. Jakobsen, *J. Magn. Reson.*, **10**, 74 (1973).
(19) R. A. Bernheim and B. J. Lavery, *J. Am. Chem. Soc.*, **89**, 1279 (1967).
(20) I. N. Bojesen, J. H. Hog, J. T. Nielsen, I. B. Petersen, and K. Schaumberg, *Acta Chem. Scand.*, **25**, 2739 (1971).
(21) (a) V. M. S. Gil and A. C. P. Alves, *Mol. Phys.*, **16**, 527 (1969); (b) NOTE ADDED IN PROOF: After acceptance of this manuscript, Thorpe et al. (*J. Magn. Reson.*, **15**, 98 (1975)) reported C-F coupling constants in some fluorinated purines. Their results are substantially consistent with ours.
(22) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4254 (1967).
(23) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 1 (1970).
(24) The geometry was taken from C. Leibovici, *J. Mol. Struct.*, **6**, 158 (1970).
(25) C. J. Jameson and M. C. Damasco, *Mol. Phys.*, **18**, 491 (1970).
(26) L. Nygaard, I. Bojesen, T. Pedersen, and J. Rastrup-Andersen, *J. Mol. Struct.*, **2**, 209 (1968).
(27) A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, **55**, 950 (1971); **58**, 4714 (1973).
(28) (a) C. S. Giam and J. L. Lyle, *J. Chem. Soc. B*, 1516 (1970); (b) C. L. Bell and S. S. Danyluk, *J. Am. Chem. Soc.*, **88**, 2344 (1966).

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XVII. Secondary Deuterium Isotope Effect and the Absence of a "Memory" in the β Scission of a Tetra-*tert*-butoxyphosphoranyl[1]

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Abstract: The reaction of tri-*tert*-butyl phosphite with *tert*-butoxy radicals yields the phosphate and a *tert*-butyl radical via an intermediate tetra-*tert*-butoxyphosphoranyl radical. Using EPR spectroscopy and deuterium labeling, it has been shown that, at temperatures from 78 to −100°, this reaction occurs without any "memory" as to which *tert*-butoxy attacked the phosphite. However, the β scission of the phosphoranyl to phosphate and *tert*-butoxy exhibits a significant secondary β-deuterium isotope effect. After correction for the isotope effect involved in the disproportionation of *tert*-butyls ($k_d^{(CH_3)_3C}/k_d^{(CD_3)_3C} = 1.4 \pm 0.2$ from 80 to −20°, it being assumed that the combination rate constants $k_c^{(CH_3)_3C}$ and $k_c^{(CD)_3C}$ are equal), the isotope effect *per deuterium* for decay of the phosphoranyl can be represented by $\log (k_\beta^H/k_\beta^D) = -0.029 + 0.063/\theta$ where $\theta = 2.3RT$ kcal/mol. These isotope effects are discussed in relation to isotope effects in analogous reactions, and the advantages in terms of sensitivity and available temperature range of our procedure are pointed out.

Trialkyl phosphites are oxidized to trialkyl phosphates by alkoxy radicals. Tetraalkoxyphosphoranyl radicals (**1**) were proposed as intermediates in this reaction many years ago,[3] and several such species have now been detected by EPR spectroscopy.[4-7]

$$R^*O\cdot + (RO)_3P \longrightarrow \underset{\textbf{1}}{R^*O\dot{P}(OR)_3} \begin{array}{l} \nearrow R^*\cdot + OP(OR)_3 \\ \searrow R\cdot + OP(OR^*)(OR)_2 \end{array} \qquad (1)$$

The question as to whether the overall reaction has any "memory" when the attacking radical, $R^*O\cdot$, and the alkoxy groups of the phosphite, RO, are identical has attracted considerable attention.[4,6,8,9] The only important experimental observations are due to Bentrude and coworkers.[8,9] At 65° with $R = (CH_3)_3C$ and $R^* = (CH_3)_3{}^{14}C$, the ^{14}C label was completely scrambled in the phosphate.[8] At the same temperature with $R = C_6H_5CH_2$ and $R^* = p\text{-}CH_3C_6H_4CH_2$ (and vice versa) the incoming benzyloxy transferred its oxygen 1.2 times as readily as the benzyloxys of the phosphite.[9] We have reinvestigated the reaction of *tert*-butoxy with tri-*tert*-butyl phosphite over a temperature range from 78 to −100° using deuterium labeling. The results show that while there is no "memory" effect, there exists a substantial deuterium isotope effect on the β scission of this phosphoranyl.

Experimental Section

The EPR apparatus, methods of sample preparation, and measurements of radical concentration have been described previously.[6,10] Tri-*tert*-butyl phosphite and its per deuterated analog were prepared by the method of Mark and Van Wazer.[11] Perdeuteriodi-*tert*-butyl peroxide was prepared from the deuterated alcohol[12] and was purified by chromatography through an alumina column, (>98% purity by VPC). All other materials were commercially available and were purified before use.

EPR samples were prepared from the deuterated phosphite, di-*tert*-butyl peroxide, and a solvent (1:1:4 v/v). Cyclopropane was used as a solvent in experiments below room temperature, and isooctane was used in the remainder. Samples were photolyzed directly in the cavity of the EPR spectrometer, and measurements of the ratio of the normal and deuterated *tert*-butyl radical concentrations, $[(CH_3)_3C\cdot]/[(CD_3)_3C\cdot]$, were made over a range of temperature. In a second set of experiments, the labeling was reversed so that the samples contained tri-*tert*-butyl phosphite and deuterated di-*tert*-butyl peroxide. Samples were photolyzed only for a short period of time in order to avoid any complications resulting from the buildup of products. Photolysis of solutions of the respective phosphites in the absence of di-*tert*-butyl peroxide did not give rise to any EPR signals.

The combination to disproportionation ratios for the self reaction of $(CH_3)_3C\cdot$ and $(CD_3)_3C\cdot$ were required for a complete kinetic analysis of the EPR data. Samples were prepared from di-*tert*-butyl peroxide and triethyl phosphite (1:1 v/v) and were photolyzed at temperatures in the range −20 to 80° until 1–5% conversion of the peroxide was obtained. The samples were then analyzed by VPC. The principal products detected were isobutylene, isobutane, and 2,2,3,3-tetramethylbutane. Small quantities of 2,2,4-trimethylpentane and 2,4,4-trimethyl-1-pentene were sometimes detected, the yield being quite sensitive to the extent of sample conversion and temperature. A similar set of experiments was carried out using perdeuterio-di-*tert*-butyl peroxide. These experiments were fewer in number because of the small quantity of deuterated peroxide available.

Results

(i) β Scission of Tetra-*tert*-butoxyphosphoranyl. Experimental Data. Photolysis of solutions of $(CD_3)_3COOC(CD_3)_3$ and $\{(CH_3)_3CO\}_3P$ in the cavity of the EPR spectrometer gave rise to the spectra of $(CD_3)_3\dot{C}$ and $(CH_3)_3\dot{C}$ radicals[13] [see reaction 1, $R^* = (CD_3)_3C$, $R = (CH_3)_3C$]. The relative concentrations of these two radicals were measured. The ratio, $[(CH_3)_3\dot{C}]/3[(CD_3)_3\dot{C}]$ (the 3 being introduced for statistical reasons), was greater than unity at all temperatures and increased with decreasing temperature (see Table I for some representative data).

These results indicate that there is *either* a positive deuterium isotope effect for β scission of the phosphoranyl radical, *or* that in its decomposition, the phosphoranyl retains a "memory" of the incoming alkoxy and preferentially retains that group.

In experiments with the labeling reversed [i.e., $(CH_3)_3COOC(CH_3)_3$ and $\{(CD_3)_3CO\}_3P$], the ratio $3[(CH_3)_3\dot{C}]/[(CD_3)_3\dot{C}]$ was also >1.0 at all temperatures and increased with decreasing temperature (see Table I).

Therefore, in its β scission, the tetra-*tert*-butoxyphosphoranyl has no "memory", but it does exhibit a substantial secondary deuterium isotope effect.

In both of the above reaction systems, and at all temperatures, the concentration of *tert*-butyl radicals (normal and deuterated) was proportional to the square root of the incident-light intensity. This indicates that all *tert*-butyls are destroyed by reaction with a second *tert*-butyl. Quantitative treatment of the EPR data is complicated by the likely occurrence of a deuterium isotope effect on this reaction. Fortunately, the magnitude of this isotope effect can be roughly estimated by comparing the individual disproportionation-combination ratios for $(CH_3)_3\dot{C}$ and for $(CD_3)_3\dot{C}$.

(ii) The *tert*-Butyl + *tert*-Butyl Reaction. The $(CH_3)_3\dot{C}$ (or $(CD_3)_3\dot{C}$) radical was generated and destroyed according to the following reaction scheme, which accounts for all of the observed products.

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3C\dot{O}$$

$$(CH_3)_3C\dot{O} + (CH_3CH_2O)_3P \longrightarrow (CH_3)_3\dot{C} + (CH_3CH_2O)_3PO$$

$$(CH_3)_3\dot{C} + (CH_3)_3\dot{C} \xrightarrow{k_c} (CH_3)_3CC(CH_3)_3$$

$$(CH_3)_3\dot{C} + (CH_3)_3\dot{C} \xrightarrow{k_d} CH_2C(CH_3)_2 + (CH_3)_3CH$$

$$(CH_3)_3\dot{C} + CH_2C(CH_3)_2 \longrightarrow (CH_3)_3CCH_2\dot{C}(CH_3)_2$$

$$(CH_3)_3\dot{C} + (CH_3)_3CCH_2\dot{C}(CH_3)_2 \longrightarrow CH_2C(CH_3)_2 + (CH_3)_3CCH_2CH(CH_3)_2$$

$$(CH_3)_3\dot{C} + (CH_3)_3CCH_2\dot{C}(CH_3)_2 \longrightarrow (CH_3)_3CH + (CH_3)_3CCH_2C(CH_3)CH_2$$

Table I. Representative Data Illustrating the Variation in the Measured Ratio, $[(CH_3)_3\dot{C}]/[(CD_3)_3\dot{C}]$, with Temperature[a]

Temp, °C	$[(CH_3)_3\dot{C}]/[(CD_3)_3\dot{C}]$	
	$(CD_3)_3C\dot{O} + [(CH_3)_3CO]_3P$	$(CH_3)_3C\dot{O} + [(CD_3)_3CO]_3P$
10	3.8	0.43
−10	4.4	0.46
−30	4.5	0.51
−50	5.1	0.59
−70	5.3	0.58

[a] Ratios are averages of at least three separate experiments. The individually measured ratios were always within 10% of the mean.

Although it was impossible to check the overall product balance at the small conversions employed (particularly since the triethyl phosphite contained traces of phosphate), this scheme can be justified via the predicted equation

$$\alpha = \frac{[(CH_3)_3CH] - [(CH_3)_3CCH_2C(CH_3)CH_2]}{[CH_2C(CH_3)_2] + [(CH_3)_3CCH_2C(CH_3)CH_2]} = 1.0$$

It can be seen from the results obtained with $(CH_3)_3\dot{C}$ and $(CD_3)_3\dot{C}$ (Tables II and III, respectively) that α is equal to 1.0 within our experimental accuracy.

According to the above scheme, the ratio of the rate constant for disproportionation to that for combination is given by:

$$\frac{(k_d)^{(CH_3)_3\dot{C}}}{(k_c)} = \frac{[(CH_3)_3CH] + [CH_2C(CH_3)_2]}{2[(CH_3)_3CC(CH_3)_3]}$$

It seems reasonable to assume that the isotope effect for combination (which is a secondary β-deuterium effect) will be negligible in comparison with the isotope effect on disproportionation (which combines a primary deuterium effect with both α- and β-deuterium secondary effects). That is, if we assume $k_c^{(CH_3)_3C} = k_c^{(CD_3)_3C}$ then the data in Table II and III yields

$$k_d^{(CH_3)_3C}/k_d^{(CD_3)_3C} = 1.4 \pm 0.2$$

over the temperature range investigated.

Although the individual k_d/k_c ratios are reasonably reliable, the derived Arrhenius type equations, viz.,

$$\log\left(\frac{k_d}{k_c}\right)^{(CH_3)_3C} = 0.46\ (\pm\ 0.2) + 1.5\ (\pm\ 0.3)/\theta$$

$$\log\left(\frac{k_d}{k_c}\right)^{(CD_3)_3C} = -0.59\ (\pm\ 0.4) + 1.5\ (\pm\ 0.6)/\theta$$

(where $\theta = 2.3RT$ kcal/mol) have high error limits because of the severely limited temperature range of these experiments.

(iii) β Scission of Tetra-*tert*-butoxyphosphoranyl. Calculation of the Isotope Effect. In the preceding section, it was shown that the bimolecular decay of $(CD_3)_3\dot{C}$ radicals probably occurs more slowly than that of $(CH_3)_3\dot{C}$ radicals. The deuterium isotope effect on β scission, which is, to a first approximation, given by the statistically adjusted $[(CH_3)_3\dot{C}]/[(CD_3)_3\dot{C}]$ ratio, must therefore be corrected to allow for the slower loss of $(CD_3)_3\dot{C}$ radicals from the system. This correction term can be derived by considering all possible *tert*-butyl + *tert*-butyl reactions and *assuming* that disproportionations involving conversion of $(CD_3)_3\dot{C}$ to $CD_2C(CD_3)_2$ occur 1.4 times more slowly than the analogous reactions involving $(CH_3)_3\dot{C}$. If the statistically adjusted $[(CH_3)_3\dot{C}]/[(CD_3)_3\dot{C}]$ ratio is represented by X and $(k_d/k_c)^{(CH_3)_3C}$ by Y, then the isotope effect per *tert-butyl* for β scission is given by[14]

$$\frac{(k_\beta)^{(CH_3)_3C}}{(k_\beta)^{(CD_3)_3C}} = X\left(\frac{(1 + X) + Y(0.86 + X)}{(1 + X) + Y(0.71 + 0.86X)}\right)$$

The isotope effect *per deuterium* is given by

$$\frac{k_\beta^{H}}{k_\beta^{D}} = \left(\frac{k_\beta^{(CH_3)_3C}}{k_\beta^{(CD_3)_3C}}\right)^{1/9}$$

Table II. Product Analysis for the Self Reaction of $(CH_3)_3\dot{C}$[a]

Temp, °C	$(CH_3)_3CH$	$CH_2C(CH_3)_2$	$(CH_3)_3CC(CH_3)_3$	$(CH_3)_3CCH_2\text{-}C(CH_3)CH_2$	α	$\left(\frac{k_d}{k_c}\right)^{(CH_3)_3C}$
80	10.3	8.6	3.2	0.45	1.09	3.0
60	12.1	10.5	3.4	0.54	1.05	3.4
40	12.4	11.4	3.4	0.31	1.04	3.6
20	9.8	10.1	2.3	0.25	0.92	4.2
0	13.4	13.1	2.3	0.01	1.01	5.6
−20	11.9	12.2	1.6	0.00	0.98	7.5

[a] Product concentrations are given in arbitrary units.

Table III. Product Analysis for the Self Reaction of $(CD_3)_3\dot{C}$[a]

Temp, °C	$(CD_3)_3CD$	$CD_2C(CD_3)_2$	$(CD_3)_3CC(CD_3)_3$	$(CD_3)_3CCD_2\text{-}C(CD_3)CD_2$	α	$\left(\frac{k_d}{k_c}\right)^{(CD_3)_3C}$
80	18.7	12.1	6.8	2.5	1.11	2.3
50	17.0	13.7	4.7	1.8	0.99	3.2
20	14.5	14.4	4.2	0.5	0.98	3.4
0	8.0	7.8	2.6	0.3	0.99	2.9
−25	13.6	13.6	2.8	0.0	1.00	4.9

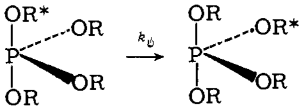
[a] Product concentrations are given in arbitrary units.

Values of log $(k_\beta{}^H/k_\beta{}^D)$ have been plotted against $1/T$ in Figure 1. Each point represents an average value obtained from three separate EPR experiments. The open circles were obtained with the $(CD_3)_3C\dot{O}$ + $[(CH_3)_3CO]_3P$ system, and the filled circles with the $(CH_3)_3C\dot{O}$ + $[(CD_3)_3CO]_3P$ system. The agreement between the two sets of data rules out any "memory" in this reaction. The data can be represented by

$$\log (k_\beta{}^H/k_\beta{}^D) = -0.029 + 0.063/\theta$$

Discussion

(i) Absence of "Memory" in the β Scission of $[(CH_3)_3CO]_4\dot{P}$. The majority of phosphoranyl radicals are generally believed to have a trigonal bipyramidal structure with two apical and two equatorial ligands.[4-7,15,16] On this basis, the absence of a "memory" effect in the formation and decomposition of tetra-*tert*-butoxyphosphoranyl can be interpreted in three ways. (a) Formation of the phosphoranyl does not occur in a stereospecific manner. (b) Apical and equatorial positions are equally reactive (somewhat unlikely since the apical bonds are probably longer than the equatorial bonds). (c) Ligand exchange by some process such as pseudorotation is rapid compared with β scission, i.e., $k_\psi \gg k_\beta$.



This last implies, of course, that the half-life for isomerization, $\tau_\psi{}^{1/2}$, must be less than the half-life of the phosphoranyl, $\tau_\beta{}^{1/2}$, which we have calculated from our earlier measurement[6] of k_β and have indicated on Figure 1. In this connection, it should be added that although $[(CH_3)_3CO]_4\dot{P}$ and other acyclic tetraalkoxyphosphoranyls show no resolvable fine structure in their EPR spectra, certain spiro tetraalkoxyphosphoranyls, e.g.,


$OCH_2CH_2O\dot{P}OCH_2CH_2O$

show different hyperfine splittings from apical and equatorial substituents.[16] This supports the view that tetraalkoxyphosphoranyls have two distinct types of ligand. The absence of hyperfine splitting from the acyclic radicals *may* indicate that their rates of ligand rearrangement are faster than the rates for the spiro phosphoranyls.

Our results with $[(CH_3)_3CO]_4\dot{P}$ support Bentrude and Wielesek's[8] pioneering study on this radical. However, the absence of a memory in this sterically crowded phosphoranyl does not imply that less hindered tetraalkoxyphosphoranyls will behave in the same way, and, in fact, certain of them do appear to retain a "memory" of their formation.[9]

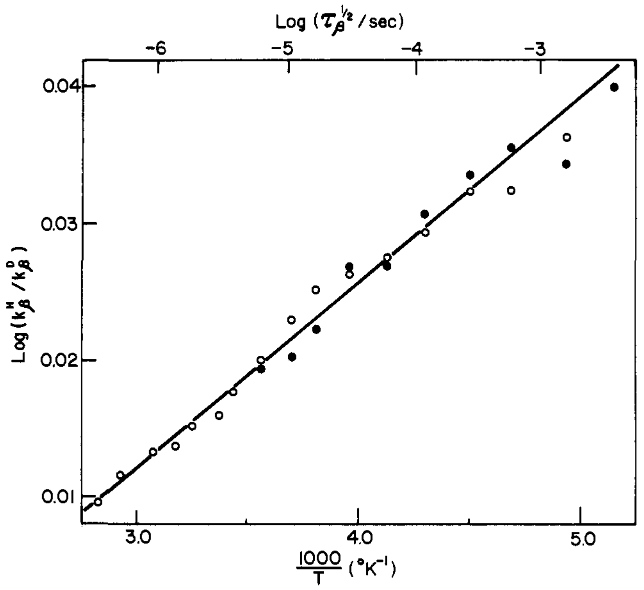


Figure 1. Variation with temperature in the isotope effect *per deuterium* for the β scission of partially deuterated tetra-*tert*-butoxyphosphoranyl: (○) $(CD_3)_3CO\dot{P}[OC(CH_3)_3]_3$; (●) $[(CD_3)_3CO]_3\dot{P}OC(CH_3)_3$. The half-life of the phosphoranyl is given on the upper scale.

(ii) Deuterium Isotope Effect in the β Scission of $[(CH_3)_3CO]_4\dot{P}$. Koenig and Wolf[17] have listed five theories that have been proposed to explain secondary β-deuterium isotope effects: (a) pure steric factors, (b) a decrease in C-H bending frequency in a hyperconjugatively stabilized transition state, (c) a decrease in C-H stretching frequency in a hyperconjugatively stabilized transition state, (d) hyperconjugative effects plus solvation, and (e) a decreased zero-point energy due to hyperconjugation and anharmonicity. Theoretical speculation on the β-deuterium effect[17,18] appears to outweigh experiment by a considerable margin, particularly experiments relating to radical-forming reactions, which appear to be confined to the decomposition of three *tert*-butyl peresters[17,19] and azobis-α-phenylethane.[20] The closest analog to the present reaction is the concerted decomposition of *tert*-butyl perpivalate, for which k_H/k_D = 1.016 per deuterium at 60°.[19] This can be compared with

$$(CH_3)_3CC(O)OOC(CH_3)_3 \longrightarrow (CH_3)_3\dot{C} + CO_2 + \dot{O}C(CH_3)_3$$

$$(CD_3)_3CC(O)OOC(CH_3)_3 \longrightarrow (CD_3)_3\dot{C} + CO_2 + \dot{O}C(CH_3)_3$$

our value of 1.028/D for $[(CH_3)_3CO]_4\dot{P}$ at 60° and with a value of 1.05/D calculated by a semiempirical molecular-orbital method for a reaction in which there is full development of the radical in the transition state.[18,21]

Previous work on secondary β-deuterium isotope effects[17,19,20] has been confined either to a single temperature or to a very narrow range of temperatures. This is unfortunate since our isotope effect increases more rapidly with decreasing temperature than is predicted by any theory.[22] That is, our experiments give $E_\beta^H - E_\beta^D = -63$ cal/mol per deuterium which is about three times the value we calculate. Furthermore, our results give $A_\beta^H/A_\beta^D = 0.935$ per deuterium, whereas theoretical treatments[22] normally suggest that $A^H/A^D = 1.0$, or *slightly more* than 1.0. While these differences between experiment and theory may seem ridiculously small, we believe they are probably outside our experimental error.[23] If this is true and is confirmed by independent experiments on other systems, then the theories of secondary β-deuterium isotope effects on radical-forming reactions should be reexamined.

(iii) The *tert*-Butyl + *tert*-Butyl Reaction. The $(k_d/k_c)^{(CH_3)_3C}$ ratios reported in Table II are in excellent agreement with the results of most previous workers who have studied this reaction (both in the gas and in the liquid phase).[24] The decrease in k_d/k_c with increasing temperature (which implies a greater temperature dependence for combination than for disproportionation) has been observed for a wide variety of radicals in solution.[24] Our value for $E_c - E_d$ (1.5 ± 0.3 kcal/mol) for *tert*-butyl is of similar magnitude to the activation energy differences reported for other radicals in solution[24] but is larger than the value reported for *tert*-butyl in the gas phase, viz.,[25] 0.25 ± 0.25 kcal/mol.

Since $E_c \neq E_d$ for *tert*-butyl, the accurate measurement of $k_d + k_c$ over a range of temperature (by, e.g., the kinetic EPR technique)[6,10] should be accompanied by measurements via products of k_d/k_c carried out (to low conversions only) over the same temperature range. If this is not done, the Arrhenius plot will be curved, and no exact significance will attach to either E_{d+c} or A_{d+c} values derived from it. These considerations also apply to other alkyl radicals.

Gibian and Corley have recently reviewed the data on deuterium isotope effects in alkyl radical-alkyl radical reactions.[24] They conclude that "*in the gas, liquid, and solid phase, there is a significant kinetic isotope effect that must be a primary one on the disproportionation.* The magnitudes of these effects are surprisingly large for reactions of such low activation energies." Our own isotope effect, $(k_d/k_c)^{(CH_3)_3C}/(k_d/k_c)^{(CD_3)_3C} = 1.4 \pm 0.2$ [which we equate with $k_d^{(CH_3)_3C}/k_d^{(CD_3)_3C}$], is of a magnitude similar to those previously reported, e.g., 1.4 for $\dot{C}_2H_5/\dot{C}_2D_5$ in the gas phase[26] and 1.87 for $C_6H_5\dot{C}HCH_3/C_6H_5\dot{C}HCD_3$ in solution.[27] Whether these isotope effects arise from activation entropy factors, i.e., $A_d^H > A_d^D$ (as our data indicate), or from energy factors, i.e., $E_d^D > E_d^H$, their existence implies that disproportionation and combination do not proceed through the same activated complex.[24]

Conclusion

Although the question regarding a "memory" in tetra-*tert*-butoxyphosphoranyl is somewhat limited, it should, we hope, be clear that the EPR and analytical methods used in this investigation could be more widely employed. The major experimental problem associated with the observation of secondary deuterium isotope effects is that the quantity to be measured is very small. Despite its limitation, it would seem that the EPR technique discussed above represents one of the most accurate approaches to this problem, and furthermore an approach that can be applied over a very wide range of temperatures.

References and Notes

(1) Issued as NRCC No. 14532. Part XVI: D. Lal, D. Griller, S. Husband, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6355 (1974).
(2) NRCC Postdoctoral Fellow 1973–1975.
(3) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **79**, 5326 (1957); **81**, 1243 (1959); C. Walling and M. S. Pearson, ibid., **86**, 2262 (1964).
(4) A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem.*, **10**, 738 (1971); *J. Chem. Soc., Perkin Trans. 2*, 993, 2225 (1972).
(5) P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 6033 (1972).
(6) G. B. Watts, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, **94**, 8784 (1972).
(7) A. G. Davies, R. W. Dennis, D. Griller, and B. P. Roberts, *J. Organomet. Chem.*, **42**, C47 (1972).
(8) W. G. Bentrude and R. A. Wielesek, *J. Am. Chem. Soc.*, **91**, 2406 (1969).
(9) W. G. Bentrude and T. B. Min, *J. Am. Chem. Soc.*, **94**, 1025 (1972).
(10) K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Am. Chem. Soc.*, **93**, 902 (1971), and subsequent papers in this series.
(11) V. Mark and J. A. Van Wazer, *J. Org. Chem.*, **29**, 1006 (1964).
(12) N. A. Milas and D. M. Surgenor, *J. Am. Chem. Soc.*, **68**, 205 (1946).
(13) At lower temperatures, $(CD_3)_3CO\dot{P}\{OC(CH_3)_3\}_3$ was also observed.
(14) The correction factor (inside the brackets) increases the isotope effect by about 20%.
(15) A. G. Davies, R. W. Dennis, D. Griller, K. U. Ingold, and B. P. Roberts, *Mol. Phys.*, **25**, 989 (1973).
(16) D. Griller and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1417 (1973).
(17) T. Koenig and R. Wolf, *J. Am. Chem. Soc.*, **89**, 2948 (1967).
(18) T. Koenig and R. Wolf, *J. Am. Chem. Soc.*, **91**, 2569 (1969).
(19) T. Koenig and R. Wolf, *J. Am. Chem. Soc.*, **91**, 2574 (1969).
(20) S. Seltzer and E. J. Hamilton, Jr., *J. Am. Chem. Soc.*, 88, 3775 (1966).
(21) In our view, such calculations are difficult to justify since a simple treatment of *tert*-butyl loss as a *primary* isotope effect involving atoms of mass 57 $[(CH_3)_3C]$ and 66 $[(CD_3)_3C]$ yields an isotope effect that is in better agreement with experiment. Thus, Melander[22] in his simple treatment relates a primary isotope effect to the fundamental stretching frequency of the bond that is cleaved by the expression $k_1/k_2 = \exp[hc(\nu_1 - \nu_2)/2kT]$. If the stretching frequency for the $(CH_3)_3C\text{–}O$, ν_1, is taken to be 1080 cm^{-1}, that for the $(CD_3)_3C\text{–}O$ bond, ν_2, will be $1080 \times (57/66)^{1/2} = 1000$ cm^{-1}.[22] At 60°, Melander's equation then yields $k_H/k_D = 1.02$ for the loss of *tert*-butyl vs. perdeuterio-*tert*-butyl.
(22) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N.Y., 1960, p 20–21.
(23) Measurements of relative radical concentrations might be in error by ±20%, and the error may vary systematically with temperature as a result of different extents of EPR line broadening for the two radicals. There is also a smaller error arising from uncertainties in correcting for the isotope effect on the *tert*-butyl + *tert*-butyl reaction.
(24) M. J. Gibian and R. C. Corley, *Chem. Rev.*, **73**, 441 (1973).
(25) D. G. L. James and R. D. Stuart, *Trans. Faraday Soc.*, **65**, 175 (1969).
(26) P. J. Boddy and E. W. R. Steacie, *Can. J. Chem.*, **38**, 1576 (1960).
(27) M. J. Gibian and R. C. Corley, *J. Am. Chem. Soc.*, **94**, 4178 (1972).