J. Org. Chem. **1996,** *61,* 4101−4106 **4101**

Equilibrium Acidities and Homolytic Bond Dissociation Enthalpies of the Acidic C−H Bonds in *P*-(*Para*-substituted benzyl)triphenylphosphonium Cations and Related Cations

Xian-Man Zhang* and Albert J. Fry*

Department of Chemistry, Wesleyan University, Middletown, Connecticut 06459

Frederick G. Bordwell*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208

Received October 16, 1995 (Revised Manuscript Received April 9, 1996[⊗]*)*

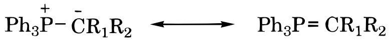
Equilibrium acidities (pK_{HA}) of six *P*-(*para*-substituted benzyl)triphenylphosphonium (p-GC_6H_4-$CH_2PPh_3^+$) cations, *P*-allyltriphenylphosphonium cation, *P*-cinnamyltriphenylphosphonium cation, and *As*-(*p*-cyanobenzyl)triphenylarsonium cation, together with the oxidation potentials [$E_{ox}(A^-)$] of their conjugate anions (ylides) have been measured in dimethyl sulfoxide (DMSO) solution. The acidifying effects of the α-triphenylphosphonium groups on the acidic C−H bonds in toluene and propene were found to be ca 25 pK_{HA} units (34 kcal/mol). Introduction of an electron-withdrawing group such as 4-NO_2, 4-CN, or 4-Br into the para position of the benzyl ring in p-$GC_6H_4CH_2PPh_3^+$ cations resulted in an additional acidity increase, but introduction of the 4-OEt electron-donating group decreases the acidity. The equilibrium acidities of p-$GC_6H_4CH_2PPh_3^+$ cations were nicely linearly correlated with the Hammett σ^- constants of the substituents (G) with a slope of 4.78 pK_{HA} units ($R^2 = 0.992$) (Figure 1). Reversible oxidation potentials of the *P*-(*para*-substituted benzyl)triphenylphosphonium ylides were obtained by fast scan cyclic voltammetry. The homolytic bond dissociation enthalpies (BDEs) of the acidic C−H bonds in these cations, estimated by combining their equilibrium acidities with the oxidation potentials of their corresponding conjugate anions, showed that the α-Ph_3P^+ groups have negligible stabilizing or destabilizing effects on the adjacent radicals. The equilibrium acidity of *As*-(*p*-cyanobenzyl)triphenylarsonium cation is 4 pK_{HA} units weaker than that of *P*-(*p*-cyanobenzyl)triphenylphosphonium cation, but the BDE of the acidic C−H bond in *As*-(*p*-cyanobenzyl)triphenylarsonium cation is ca 2 kcal/mol higher than that in *P*-(*p*-cyanobenzyl)triphenylphosphonium cation.

Introduction

Phosphonium ylides (Wittig reagents) derived from α-substituted triphenylphosphonium cations by removal of the α-proton are important reactive intermediates (synthons) in synthetic organic chemistry for the conversion of carbonyl groups (>C═O) in aldehydes or ketones into the corresponding C═C groups.[1] The phosphonium ylide structure is generally believed to be the hybrid of the covalent and dipolar canonical structures as shown in Scheme 1.[1a,b]

The α-proton in *P*-substituted triphenylphosphonium cations are known to be readily deprotonated by weak base even in aqueous solutions since the α-triphenylphosphonium group (α-Ph_3P^+) is one of the strongest known acidifying groups.[2−4] For example, *P*-acetonyltriphenylphosphonium cation was found to have pK_{HA} value of 6.5 in 80% $EtOH/H_2O$.[3] *P*-Phenacyltriphenylphosphonium cation was reported to have pK_{HA} values of 6.0 and 5.6 in 80% $EtOH/H_2O$[3] and 95% $EtOH/H_2O$,[4a] respectively. The pK_{HA} value for *P*-(9-fluorenyl)triphenylphosphonium cation was determined to be 7.5 in 31% water/dioxane.[4b]

Scheme 1



$$Ph_3\overset{+}{P}-\overset{-}{C}R_1R_2 \longleftrightarrow Ph_3P{=}CR_1R_2$$

The extremely large acidifying effects of the α-triphenylphosphonium groups at one time were believed to be caused by a combination of the coulombic effects of the positive charge on the phosphorus atom and the resonance delocalization of the negative charge into the available 3d vacant orbitals of phosphorus. The postulated resonance stabilization was supported by the near planar carbanion structure of the stabilized ylides as determined by X-ray diffraction.[5] However, the carbanions of the ylides derived from nonstabilized triphenylphosphonium cations such as *P*-methyltriphenylphosphonium and *P*-cyclopropyltriphenylphosphonium cations were found to be pyramidal.[6] The chemical shifts of ^1H, ^{13}C, and ^{31}P NMR studies of several phosphonium ylides showed that the dominant structure is the dipolar P^+−C^- zwitterion rather than the P═C double bond (Scheme 1).[7] Furthermore, molecular orbital calculations cast

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[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1996.

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(4) (a) Johnson, A. W.; Amel, R. T. *Can. J. Chem.* **1968**, *46*, 461−463. (b) Johnson, A. W.; LaCount, R. B. *Tetrahedron* **1960**, *9*, 130.

(5) (a) Mak, T. C. W.; Trotter, J. *Acta Crystallogr.* **1965**, *18*, 81−99. (b) Stephens, F. S. *J. Chem. Soc.* **1965**, 5640−5650. (c) Stephens, F. S. *J. Chem. Soc.* **1965**, 5658−5678. (d) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(6) (a) Schmidbaur, H.; Schier, A. S.; Milewski-Mahrla, B.; Schubert, U. *Chem. Ber.* **1982**, *115*, 722−731. (b) Schmidbaur, H.; Schier, A. S.; Frazao, C. M. F.; Muller, G. *J. Am. Chem. Soc.* **1986**, *108*, 976. (c) Schmidbaur, H.; Schier, A. S.; Neugebauer, D. *Chem. Ber.* **1983**, *116*, 2173. (d) Schmidbaur, H.; Jeong, J.; Schier, A.; Graf, W.; Wilkinson, D. L.; Muller, G.; Kruger, C. *New J. Chem.* **1989**, *13*, 341.

(7) Schlosser, M.; Jenny, T.; Schaub, B. *Heteroatom Chem.* **1990**, *1*, 151−156.

S0022-3263(95)01862-7 CCC: $12.00

doubt on the $d_\pi - p_\pi$ resonance interaction (P=C).[8] Recently, we found that seven *P*-α-substituted triphenylphosphonium cations were 9−20 pK_{HA} units (12.5−27.5 kcal/mol) more acidic than those of the corresponding *N*-α-substituted trimethylammonium cations.[9] We concluded that the much larger acidifying effects of the α-triphenylphosphonium groups than those of the α-trimethylammonium groups were caused by the larger polarizability effects of the α-triphenylphosphonium groups rather than the resonance stabilization of the negative charge into the available 3d vacant orbitals of phosphorus. The latter is unlikely because the α-triphenylphosphonium groups have no stabilization effects on the adjacent carbon radicals, as judged by the homolytic bond dissociation enthalpies of the corresponding acidic C−H bonds as estimated by combination (eq 1) of the equilibrium acidities with the oxidation potentials of the conjugate anions.[9] This is consistent with the much larger polarizability of phosphorus than nitrogen.[10] The larger polarizability effects of phenyl groups than that of the methyl groups are expected to make an additional contribution to the much larger acidifying effect of the α-triphenylphosphonium group relative to the α-trimethylammonium group.[4] For example, about 2 pK_{HA} unit increase in equilibrium acidity has been observed for the replacement of the methyl group in $MeXCH_2G$ by a phenyl group (where X = CH_2, S, O, and SO_2, and G = fluorenyl, cyanomethyl, and phenacyl, etc.).[11] The replacement of the methyl groups by phenyl groups for 9-*tert*-butylfluorene, 9-trimethylsilylfluorene, and α-trimethylsilylmethyl phenyl sulfone was also found to increase the equilibrium acidities by about 3−6 pK_{HA} units, i.e. about 1−2 pK_{HA} units for each replacement of a methyl group by a phenyl group.[12a]

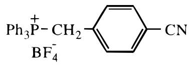
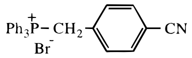
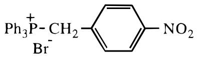
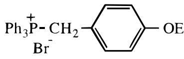
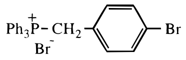
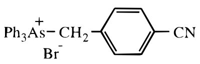
$$BDE_{HA} = 1.37\ pK_{HA} + 23.1E_{ox}(A^-) + 73.3 \quad (1)$$

Equation 1 was derived from a thermodynamic cycle, and the BDE_{HA} values estimated using eq 1 have been shown to agree with the best literature BDE values within to ±2 kcal/mol.[12b] In the present paper we extend our studies of the effects of the α-triphenylphosphonium groups on equilibrium acidities and homolytic bond dissociation enthalpies to additional substrates. The substituent effects on the equilibrium acidities and homolytic bond dissociation enthalpies of the benzylic C−H bonds are then compared with those of the acidic S−H bonds in thiophenols, the N−H bonds in anilines, and the O−H bonds in phenols.

Results and Discussion

Equilibrium Acidities. The equilibrium acidities of six *P*-(*para*-substituted benzyl)triphenylphosphonium (p-$GC_6H_4CH_2PPh_3^+$) cations, *P*-allyltriphenylphosphonium cation, *P*-cinnamyltriphenylphosphonium cation, and *As*-(*p*-cyanobenzyl)triphenylarsonium cation were measured in dimethyl sulfoxide (DMSO) solution by the overlapping indicator titration method.[13] The deviations caused by the activity coefficients of the triphenylphosphonium cations and the indicator anions have been shown to be smaller than the accepted experimental error (±0.1 p*K* units[13]) for the overlapping indicator titration method (see Appendix).

Table 1. Equilibrium Acidities and Homolytic Bond Dissociation Enthalpies of the Acidic C−H Bonds in *P*-(*Para*-substituted benzyl)triphenylphosphonium Cations and Related Cations

acids	pK_{HA}[a]	$E_{ox}(A^-)$[c]	BDE_{HA}[f]
CH_3Ph	~43[b]	-1.935[d]	88
$Ph_3P^+CH_2Ph\ Cl^-$	17.4[b]	-0.381[e]	89.3
	13.0	-0.070[e]	89.5
	13.0	-0.072[e]	89.4
	11.0	0.058[e]	89.8
	18.8	-0.529[e]	86.8
	16.4	-0.273[e]	89.5
$CH_2=CHCH_3$	~43[b]		86.6[g]
$Ph_3P^+CH_2CH=CH_2\ Br^-$	18.5	-0.550	85.9
$Ph_3P^+CH_2CH=CHPh\ Cl^-$	15.6	-0.593	81.0
	17.0	-0.221	91.5

[a] This study unless otherwise indicated. Equilibrium acidities measured in DMSO solution by the overlapping indicator titration method.[13] [b] Reference 13b. [c] Irreversible oxidation potentials in DMSO measured by conventional cyclic voltammetry unless otherwised indicated. [d] Jaun, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741. This value was estimated from the measurement in THF−HMPA (v/v, 9:1), but is consistent with the reduction potential of the benzyl radical [Sim, B. A.; Milne, P. H.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1990**, *112*, 6635]. [e] Reversible oxidation potentials measured by fast-scan cyclic voltammetry. [f] Homolytic bond dissociation enthalpies of the acidic C−H bonds estimated by using eq 1. [g] Reference 24.

All of the conjugated anions (ylides) derived from the triphenylphosphonium and triphenylarsonium cations reported in the present paper are stable enough to allow three-point titrations to be made under the experimental conditions of measurement. The results are summarized in Table 1. The equilibrium acidities of toluene and propene are too weak to be measured in DMSO solution by our titration method, but the corresponding estimated values were listed in Table 1 for comparision.

Examination of Table 1 shows that the equilibrium acidity of *P*-benzyltriphenylphosphonium cation is 25.6 pK_{HA} units stronger than that of toluene in DMSO solution. Introduction of 4-bromo, 4-cyano, and 4-nitro electron withdrawing groups into the para position of the benzyl ring in p-$GC_6H_4CH_2PPh_3^+$ cations *increases* the equilibrium acidity by 1, 4.4, and 6.4 pK_{HA} units, respec-

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(8) (a) Rank, A.; Allen, L. C.; Mislow, K. *Angew. Chem.* **1970**, *82*, 453. (b) Brill, T. B. *J. Chem. Educ.* **1973**, *50*, 392. (c) Bernardi, F.; Csizmadia, I. G.; Mangini, A.; Schlegel, H. B.; Wangbo, M. H.; Wolfe, S. *J. Am. Chem. Soc.* **1975**, *97*, 2209. (d) Lischka, H. *J. Am. Chem. Soc.* **1977**, *99*, 353. (e) Lehn, J. M.; Wipff, G. *J. Am. Chem. Soc.* **1976**, *98*, 7498. (f) Streitwieser, A.; Rajca, A.; McDowell, R. S.; Glaser, R. *J. Am. Chem. Soc.* **1987**, *109*, 4184. (g) Frand, M. M.; Pellow, R. C.; Allen, L. C. *J. Am. Chem. Soc.* **1988**, *110*, 3723. (h) Bachrach, S. M. *J. Org. Chem.* **1992**, *57*, 4367.

(9) Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1994**, *116*, 968−972.

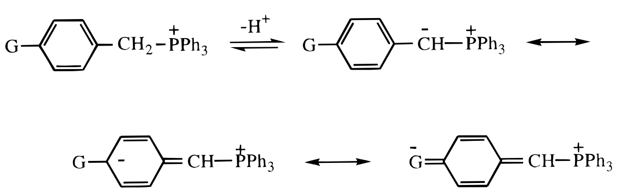
(10) (a) The dipole polarizabilities of phosphorus and nitrogen are 24.5 and 7.4 (in atomic units), respectively. (b) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272−295.

(11) Bordwell, F. G.; Zhang, X.-M. *J. Am. Chem. Soc.* **1994**, *116*, 973−976.

(12) (a) Zhang, S.; Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1995**, *117*, 602−606. (b) Bordwell, F. G.; Zhang, X.-M. *Acc. Chem. Res.* **1993**, *26*, 510−517.

(13) (a) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. D.; Drucker, G. E.; Margolin, Z.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006−7014. (b) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456 and the references cited therein.

Scheme 2



tively, but introduction of 4-ethoxy electron-donating group *decreases* the equilibrium acidity by 1.4 pK_{HA} units. The equilibrium acidities of the *P*-(*para*-substituted benzyl)triphenylphosphonium cations were found to have much better linear correlation with Hammett σ^- constants than with Hammett σ_p constants as shown in Figure 1. The slope for the linear correlation with the Hammett σ^- constants is 4.78 pK_{HA} units ($R^2 = 0.992$). It is understandable since the Hammett σ^- constants were developed for the systems where strong resonance interaction occurs between the reaction center and substituent. Similar linear correlations of the equilibrium acidities with the Hammett σ^- constants have also been observed for phenols,[14] thiophenols,[15] anilines,[16] 10-substituted-9-methylanthracenes,[17] toluenes,[18] etc.[13b] The slope of the Hammett σ^- correlation of the equilibrium acidities for *P*-(*para*-substituted benzyl)triphenylphosphonium cations is much smaller than those for toluenes (12 pK_{HA} units)[18] and 10-substituted-9-methylanthracenes (10 pK_{HA} units).[17] Clearly, the relatively smaller slope of the Hammett correlation for *P*-(*para*-substituted benzyl)triphenylphosphonium cations is associated with the coulombic and polarizability stabilization effects caused by the α-triphenylphosphonium groups on the adjacent negative charge as shown in Scheme 2. As a consequence, the resonance delocalization of the negative charge into the substituent G is diminished accordingly. Relative smaller slopes for this type linear correlations were also observed for phenylacetonitriles and benzyl phenyl sulfones.[13b]

Introduction of an α-triphenylphosphonium group into propene increases the equilibrium acidity by 24.5 pK_{HA} units, which is comparable to that for introduction of an α-triphenylphosphonium group into toluene (Table 1). But introduction of an additional phenyl group (*P*-cinnamyltriphenylphosphonium cation) increases the acidity by *only* 2.9 pK_{HA} units, which is less than half of those for the introduction of an α-phenyl group into acetone (6.7 pK_{HA} units), acetophenone (7.0 pK_{HA} units), and acetonitrile (9.4 pK_{HA} units).[13b] On the basis of ^1H, ^{13}C, and ^{31}P NMR chemical shift measurements for several phosphonium ylides, Schlosser et al.[7] has concluded that the resonance structure **1a** contributes approximately three times more to the overall electronic distribution than the resonance structure **1b** as shown in Scheme 3. In other words, the negative charge in **1** was mainly localized on α-carbon atom rather than equally localized at α- and γ-carbon atoms. This explains why the introduction of a phenyl group into the γ-carbon atom of **1** results in a relative smaller acidifying effects than expected.

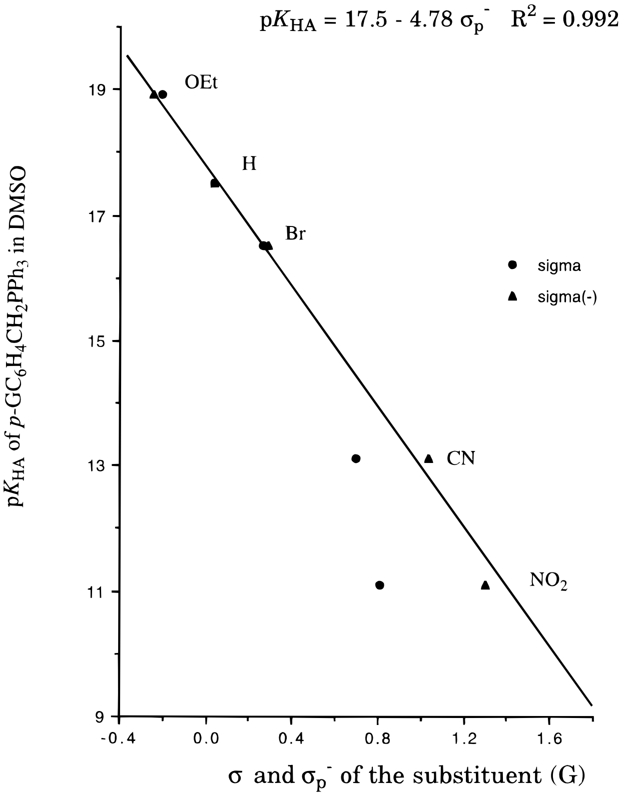
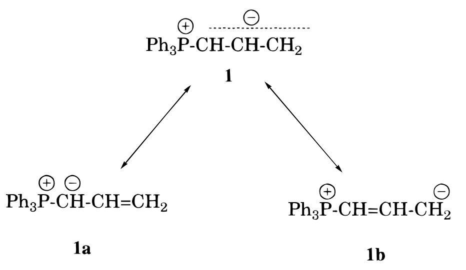


Figure 1. Correlation of the equilibrium acidities of *P*-(*para*-substituted benzyl)triphenylphosphonium cations measured in DMSO solution against Hammett σ and σ_p constants of the substituents (Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−169).

Scheme 3



The equilibrium acidity of *As*-(*p*-cyanobenzyl)triphenylarsonium cation was found to be 4 pK_{HA} units weaker than that of *P*-(*p*-cyanobenzyl)triphenylphosphonium cation. The positive charge density (electronegativity) of phosphonium group is expected to be larger than that of the corresponding arsonium group due to the relative smaller size of phosphorus atom than that of the arsenic atom,[4] which leads to smaller field/inductive (electrostatic) interaction between the positive arsenic atom and the ylidic carbanion center even though the dipolar polarizability of arsenic (29.1 in atomic unit) is larger than that of phosphorus (24.5 in atomic unit).[10b]

Oxidation Potentials. The oxidation potentials of the most conjugate anions determined by conventional cyclic voltammetry (scan rate: 0.1 V/s) were shown to be irreversible.[12b,19] The homolytic bond dissociation

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[14] Bordwell, F. G.; McCallum, R.; Olmstead, W. N. *J. Org. Chem.* **1984**, *49*, 1424.

[15] Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1982**, *47*, 3224.

[16] Bordwell, F. G., Zhang, X.-M.; Cheng, J.-P. *J. Org. Chem.* **1993**, *58*, 6410−6416.

[17] Zhang, X.-M.; Bordwell, F. G.; Bares, J. E.; Cheng, J.-P.; Petrie, B. C. *J. Org. Chem.* **1993**, *58*, 3051−3059.

[18] (a) Bordwell, F. G.; Algrim, D.; Vanier, N. R. *J. Org. Chem.* **1977**, *42*, 1817. (b) Sim, B. A.; Milne, P. H.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1990**, *112*, 6635.

[19] Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X.-M. *J. Am. Chem. Soc.* **1991**, *113*, 9790−9795.

Table 2. Reversible Oxidation Potentials of the *P*-(9-Fluorenyl)triphenylphosphonium Ylide Measured by Fast Scan Cyclic Voltammetry

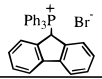
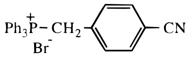
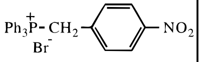
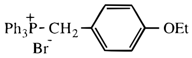
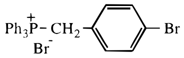
scan rate	ΔE^{b}	$E_{1/2}{}^{c}$
0.1	none	−0.041[d]
200	71	−0.0225
400	66	−0.021
1000	130	−0.032
2000	149	−0.0245
3000	288	−0.024
4000	276	−0.025
4800	375	−0.020

[a] In V/s. [b] The diferences between the two redox peaks for the reversible oxidation potentials; in mV. [c] Reversible oxidation potential of the *P*-(9-fluorenyl)triphenylphosphonium ylide; In V. [d] Irreversible oxidation potential determined by conventional cyclic voltammetry.

enthalpies estimated with the irreversible oxidation potentials by using eq 1 have been shown, however, to be in remarkable agreement with the available best literature BDE values to within ±2 kcal/mol,[12b,19] indicating that the differences of the irreversible with the reversible oxidation potentials should be less than ±100 mV (±2 kcal/mol) because the equilibrium acidities are known to be accurate to ±0.1 pK_{HA} units (0.15 kcal/mol).[13] The reversible oxidation potentials in a number of instances of nitranions determined by second harmonic alternating current voltammetry (SHACV)[19] or fast-scan cyclic voltammetry[20] have been shown to agree with the irreversible oxidation potentials obtained by conventional cyclic voltammtry to within ±50 mV. The irreversible oxidation potentials for these nitranions were found to be nicely linearly correlated with the reversible oxidation potentials with a slope of unity.[20b] But most of the carbon radicals derived from the carbanions we have studied were too reactive to be reduced back to the corresponding anions under the conditions of conventional cyclic voltammetry or even fast-scan cyclic voltammetry (scan rate up to 2000 V/s) because of their short lifetimes.[21] In an earlier paper,[9] we have pointed out that the carbon radical derived from the *P*-(9-fluorenyl)triphenylphosphonium ylide is stable enough to be reduced back to the corresponding ylide by fast-scan cyclic voltammetry presumbly because of the large steric effects of the α-triphenylphosphonium group, which retards the radical dimerization and increases its lifetime. Inspection of Table 2 shows that the reversible oxidation potential of the *P*-(9-fluorenyl)triphenylphosphonium ylide was also independent of the scan rates from 200 to 4800 V/s even though the peak potential differences (ΔE) between the two reversible redox peaks increase as the scan rates increase. Interestingly, the oxidation potentials of the *P*-(*para*-substituted benzyl)triphenylphosphonium ylides were also found to be reversible by fast-scan cyclic voltammetry, and the results are summarized in Table 3.

Examination of Tables 2 and 3 shows that the differences between the reversible and irreversible oxidation potentials for these ylides we have studied are all less than 0.050 V (~1 kcal/mol), indicating the $\mathrm{BDE_{HA}}$s estimated by using eq 1 are reliable[12b,19] even though irreversible oxidation potentials of the conjugate anions were used.

Table 3. Irreversible and Reversible Oxidation Potentials of the *P*-(9-Fluorenyl)triphenylphosphonium Ylide and *P*-(*Para*-substituted benzyl)triphenylphosphonium Ylides[a]

phosphonium cations	$E_{ox}(A^-)_{irrev}{}^{b}$	$E_{ox}(A^-)_{1/2}{}^{c}$	scan-rate[d]	ΔE^{e}
	-0.041	-0.021	400	0.020
$Ph_3P^+CH_2Ph$	-0.381	-0.339	850	0.041
	-0.072	-0.067	718	0.005
	0.050	0.058	718	0.008
	-0.527	-0.529	718	-0.002
	-0.262	-0.273	814	-0.011

[a] The phosphonium ylides were commercially samples or formed *in situ* by addition of appropriate amount of weak base into the corresponding triphenylphosphonium cation solutions. [b] Irreversible oxidation potentials measured in DMSO solution by conventional cyclic voltammetry (scan rate: 0.1 V/s); in V. [c] Reversible oxidation potentials in DMSO measured by fast-scan cyclic voltammetry; in V. [d] In V/s. [e] The differences between the reversible and irreversible oxidation potentials of the phosphonium ylides; in V.

Homolytic Bond Dissociation Enthalpies of the Acidic C−H Bonds in *P*-(*p*-Substituted benzyl)-triphenylphosphonium Cations and Related Cations. The $\mathrm{BDE_{HA}}$s of the six *P*-(*para*-substituted benzyl)triphenylphosphonium cations and three other related cations estimated from their equilibrium acidities and the oxidation potentials of their conjugate anions according to eq 1 are also summarized in Table 1.

We have shown that the BDE values of the acidic C−H bonds remain virtually constant within to the experimental error (±2 kcal/mol) for the introduction of an α-triphenylphosphonium group into the acidic sites for seven different substrates.[9] Examination of Table 1 shows that the $\mathrm{BDE_{C-H}}$ value of *P*-benzyltriphenylphosphonium cation is slightly higher than the $\mathrm{BDE_{C-H}}$ value of toluene, but it still falls within the experimental error (±2 kcal/mol). The conclusion of no stabilization effects of the α-triphenylphosphonium groups on the benzylic radicals were further supported by the essential same $\mathrm{BDE_{C-H}}$ value (89.5 ± 0.5 kcal) for the introduction of electron-withdrawing groups (4-NO_2, 4-CN, and 4-Br) into the para-position of the benzyl ring. A plot of $E_{ox}(A^-)$ vs pK_{HA} for the *P-(para*-substituted benzyl)triphenylphosphonium cations gave a nice linear correlation ($R^2 = 0.985$) as shown in Figure 2. Similar linear correlations have been observed for many other families of weak acids.[9,16,17]

The $\mathrm{BDE_{C-H}}$ values of the *P*-benzyltriphenylphosphonium cations bearing electron acceptor groups at the para-positions were shown to be linearly correlated with Hammett constants (σ_p) of the substituents with a slope of only about 0.4 kcal/mol as shown in Figure 3. Similar linear Hammett correlations, but with much *larger* slopes, have also been observed for the BDE values of the acidic H−S bonds in thiophenols, the acidic N−H

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(20) (a) Arnett, E. M.; Harvey, N. G.; Amarnath, K.; Venimadhaven, S. *J. Am. Chem. Soc.* **1990**, *112*, 7346. (b) Bordwell, F. G.; Harrelson, J. A., Jr.; Lynch, T.-Y. *J. Org. Chem.* **1990**, *55*, 3337−3341.

(21) Bausch, M. J.; Gostowski, R. *J. Org. Chem.* **1991**, *56*, 6260.

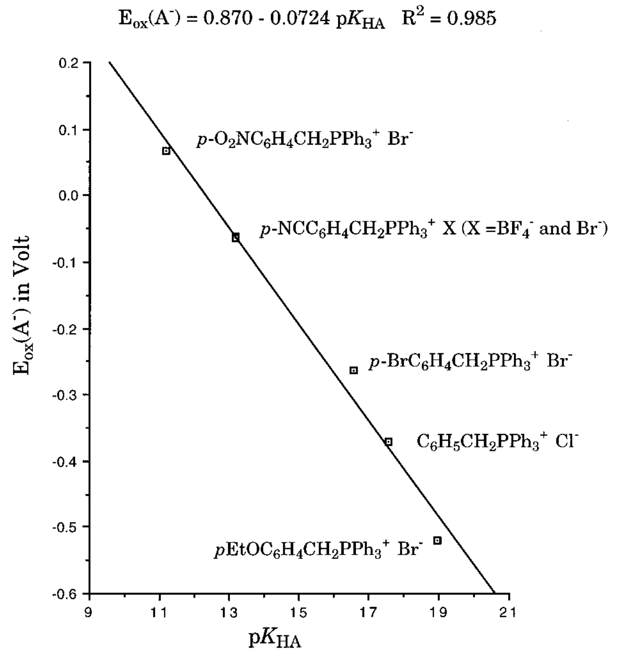


Figure 2. Plot of the oxidation potentials of the ylides derived from p-$GC_6H_4CH_2PPh^{3+}$ cations versus their equilibrium acidities in DMSO.

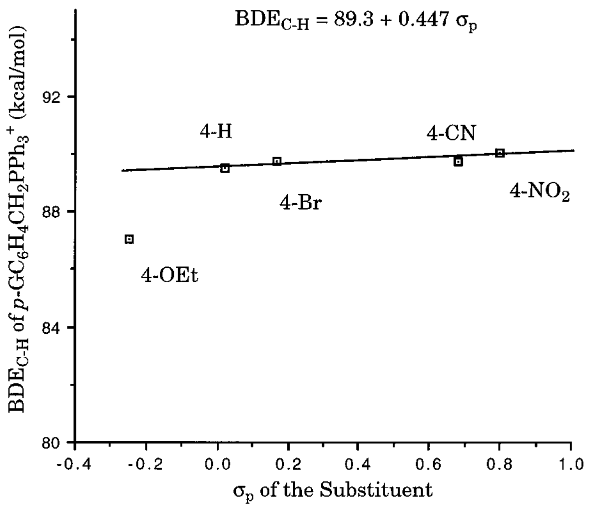
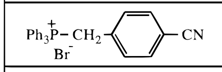
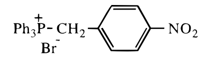
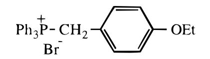
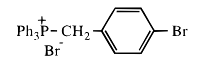
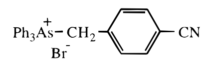


Figure 3. Hammett Plot of the BDE_{C-H} values of p-GC_6H_4-$CH_2{}^+PPh_3$ cations against the σ_p constants of substituents (Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−169).

bonds in anilines, and the acidic O−H bonds in phenols.[22] The much smaller slopes (near zero) for the BDEs of the C−H bonds can be attributed to the less polar C−H bond and the negligible ground state effects of the carbon−hydrogen bond caused by the dipolar−dipolar interactions. Because the slopes for the different Hammett correlations of the BDEs were nicely linearly correlated with the electronegativity differences between the two atoms being cleaved, the ground-state energy was mainly influenced by the dipole−dipole interaction.[23]

Introduction of an electon-donating 4-EtO group in p-$GC_6H_4CH_2PPh_3{}^+$ cation causes a derivation from the line (Figure 3) of ca. 3 kcal/mol, which can be attributed to the resonance delocalization effects of the unpaired electron in the product radical by the electron donating EtO group.[23] The BDE_{C-H} (85.9 kcal/mol) of *P*-allyltriphenylphosphonium cation was found to be essentially same as that (86.6 kcal/mol) of propene.[23] The 4.9 kcal/mol lower BDE_{C-H} value for *P*-cinnamyltriphenylphosphonium cation than that for *P*-allyltriphenylphosphonium cation is due to the delocalization of the unpaired electron into the aromatic ring. This value is close to the 5.5 kcal/mol lower BDE_{C-H} value for 9-phenylfluorene than fluorene,[19] indicating that the unpaired electron of the radical derived from *P*-allyltriphenylphosphonium ylide is presumbly equally localized at the at α- and γ-carbon atoms. The BDE_{C-H} value of *As*-(*p*-cyanobenzyl)triphenylarsonium cation is ca. 2 kcal/mol higher than that of *P*-(*p*-cyanobenzyl)triphenylphosphonium cation.

Table 4. Equilibrium Acidities Determined in DMSO Solution by the Overlapping Indicator Method[a]

cations	pK_{HA}	indicator	$pK_{IN}{}^{j}$	SDV[k]	runs	selected pK_{HA}
	13.03 13.04	HZFO2[b] HZF[c]	14.15 14.95	0.06 0.955	1 1	13.0
	11.04	9COMFH[d]	10.35	0.017	2	11.0
	18.75 18.7	CNAH[e] FMY30[f]	18.9 18.1	0.009 0.050	2 1	18.8
	16.4 16.5	HZF PFH[g]	14.95 17.9	0.08 0.06	1 1	16.4
$Ph_3P^+CH_2CH{=}CH_2\ Br^-$	18.49	CNAH	18.9	0.059	2	18.5
$Ph_3P^+CH_2CH{=}CHPh\ Cl^-$	15.63	DEPM[h]	16.5	0.035	2	15.6
	16.89 17.1	MCLPFH[i] PFH	16.8 17.9	0.007 0.07	1 1	17.0

[a] See Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456 and references cited therein. [b] 9-Fluorenone, 2-(chlorophenyl)hydrazine. [c] 9-Fluorenone, phenylhydrazine. [d] 9-(Methoxycarbonyl)fluorene. [e] 4-Chloro-2-nitroaniline. [f] 2-(Phenylsulfonyl)fluorene. [g] 9-Phenylfluorene. [h] Diethyl (*p*-methylphenyl)malonate. [i] 9-(*m*-Chlorophenyl)fluorene. [j] The pK_{HA} values of the indicators used. [k] Standard deviation of the corresponding measurement.

Experimental Section

Materials. All halides of the triphenylphosphonium cations were commercially available (Aldrich) and used as received without further purification. The oxidation potentials of the conjugate anions (ylides) derived from the onium cations investigated in this study are much negative than those of bromide and chloride ions, so the presence of these halide counterions (Cl^- and Br^-) will not interfere with the oxidation potential measurements of the onium ylides.

The equilibrium acidities in DMSO solution were measured in the room temperature by the overlapping indicator titration method as described previously.[13a] The detailed acid measurement data are summarized in Table 4. The irreversible oxidation potentials of the onium ylides were measured by conventional cyclic voltammetry as described previously.[19] The working electrode consisted of a 1.5 mm diameter platinum disc embedded in a cobalt glass seal. It was polished with 0.05 μm Fisher polishing aluminum or cleaned with an ultrasonic instrument, rinsed with ethanol, and dried before each run. The counter electrode was platinum wire (BAS). The reference electrode was Ag/AgI, but the reported oxidation potentials are all referenced to the ferrocenium−ferrocene couple ($E_{1/2}$ = 0.875 V vs the Ag/AgI couple in our instrument).[12b,19] The reversible oxidation potentials were measured by fast-scan cyclic voltammetry. A microelectrode was used as working electrode for the reversible oxidation potential measurements.

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(22) Satish, A. V. Unpublished results.

(23) Bordwell, F. G.; Zhang, X.-M.; Satish, A. V.; Cheng, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 6605−6610.

Acknowledgment. This research was supported by the National Science Foundation.

Appendix

Determination of the equilibrium acidities of a neutral weak acid (HA) by the overlapping indicator titration method may be expressed by eq 2.[13]

$$\mathrm{HA} + \mathrm{In^-} \rightleftharpoons \mathrm{HIn} + \mathrm{A^-} \qquad (2)$$

Both sides of eq 2 involve a neutral compound and an anion. In dilute solution, the activity coefficients for the neutral and ionic species in both sides of eq 2 will be approximately same and will cancel with each other.[24] In other words, we can use the molar concentrations instead of the activities to calculate the equilibrium constants.

Determination of the equilibrium acidties of the triphenylphosphonium cations in DMSO solution by the overlapping indicator titration method,[13] however, involves a triphenylphosphonium cation and an indicator anion on one side and two "neutral" molecules on the other side as shown in eq 3. Therefore, the editor and one of the reviewers suspected that the activity coefficients of the ionic species might play a *significant* role for the equilibrium acidiy measurements of the triphenylphosphonium cations.

$$\mathrm{RCH_2\overset{+}{P}{+}} + \mathrm{In^-} \rightleftharpoons \mathrm{HIn} + \mathrm{R\overset{-}{C}H\overset{+}{P}{+}Ph_3} \qquad (3)$$

In dilute solution, the activity coefficients (γ_i) of the neutral molecules should be close to unity. The activity coefficients (γ_i) of the ionic species can be determined from the Debye−Hückel method (eqs 4 and 5), which is based on calculation of the interionic force.[25] where z_i is

$$\log \gamma_i = A z_i^2 I^{1/2} \qquad (4)$$

$$A = (5.767 \times 10^4) \mathrm{M_{solv}}^{1/2} \kappa^{-3/2} T^{-3/2} \qquad (5)$$

the charge number of the ionic species, I is the ionic strength, M_{solv} is mass (kg/m^3) of the solvent used, κ is the dielectric constant of the solvent used, and T is the temperature (K).

The ionic strength (I) for our acidity measurement is about 0.001 mol/L in DMSO solution,[13] $M_{solv} = 1101$ kg/m^3, $\kappa = 46.7$. The measurements were carried out at room temperature (298.15 K). The number A and log γ_i are calculated to be 1.16 and −0.037 according to eqs 5 and 4, respectively. In other words, the maximum deviation for the equilibrium acidities caused by the activity coefficients of the ionic species will be $2 \times \log \gamma_i = 0.074$ pK units. In fact, the real deviation is expected to be even smaller than 0.074 pK units since the sizes of the triphenylphosphonium cations and the indicator anions used are much larger than those of the common ionic species such as inorganic ions. This implies that the electrostatic interactions between these organic ions in our measurements might be much smaller than that calculated from the Debye−Hückel method. On the other hand, the triphenylphosphonium ylide is dipolar rather than neutral double covalent structure (Scheme 1), which will probably cancel some of the deviation caused by the activity coefficients of the triphenylphosphonium cation and the indicator anion. Therefore, we conclude that the deviation caused by the activity coefficients of ionic species in the present and the other related studies is smaller than ±0.1 pK units.

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[24] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

[25] Reference 1b, p 235.

[26] Alberty, R. A. *Physical Chemistry*, 6th ed.; Wiley: New York, 1983; pp 219−221.