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Effects of Adjacent Onium Cations and Remote Substituents on the H−A$^+$ Bond Equilibrium Acidities in Dimethyl Sulfoxide Solution. An Extensive Ylide Thermodynamic Stability Scale and Implication for the Importance of Resonance Effect on Ylide Stabilities

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The equilibrium acidities (pK_as) of six families of remotely substituted benzyl onium salts (i.e., 4-G-$C_6H_4CH_2$-$E^+\cdot Br^-$, where $E^+ = Ph_3P^+$, Ph_2PO, Et_3N^+, Me_2S^+, Me_2Se^+, and Bu_2Te^+ and G = H, Me, CF_3, CO_2Me, CN, and NO_2), one family of α-E^+ substituted acetophenones (i.e., $PhCOCH_2$-$E^+\cdot Br^-$, where $E^+ = Me_2S^+$, Bu_2Te^+, Bu_3P^+, and Ph_3As^+), and one family of 9-E^+-substituted fluorenes (i.e., 9-E^+-FlH$\cdot Br^-$, where $E^+ = Bu_2S^+$, Me_2Se^+, Bu_2Te^+, Bu_3P^+, and Ph_3As^+) have been determined in a *single* solvent, dimethyl sulfoxide (DMSO). This allowed meaningful comparisons of the thermodynamic stabilities for an extensive range of Group VB and VIB ylides covering up to six elements (N, P, As; S, Se, Te) to be made for the first time on the basis of a unified standard. A comparison of the pK_a values of onium salts with those of their parents shows that all the onium substituents studied in the present work are strongly ylide-stabilizing, covering an anion stabilization energy range of 17−35 kcal/mol (i.e., ΔpK = 12−25 pK units). A further examination of the pK_a values also reveals that the thermodynamic stabilities of the Group VB onium ylides are in a decreasing order of $P^+{-}C^- > As^+{-}C^- > N^+{-}C^-$ and of the Group VIB onium ylides in a decreasing order of $S^+{-}C^- > Se^+{-}C^- \sim Te^+{-}C^-$, if the substituents on the onium atoms are kept similar. The stability order for the ylides of the third-row elements was found to be $S^+{-}C^- > P^+{-}C^-$, as implied by the ΔpKs of 1.7−4.2 for the three $R_3P^+{-}C^-/R_2S^+{-}C^-$ pairs compared (see text). The pK_as of the eight remotely substituted E^+-CH_2Ar series all correlate well with the σ^- constants (see Table 3) with a decreasing order of slopes as (E^+ =) $Ph_2P(O)$ (−5.86) > Ph_3As^+ (−5.35) > Bu_3P^+ (−5.00) > Ph_3P^+(−4.46) and Bu_2Te^+ (−5.50) > Me_2Se^+ (−5.03) > Me_2S^+ (−3.40), suggesting a similar trend for the extent of charge localization at the carbanions next to the E^+ group. All these observations are consistent with the assumption that at least part of the gained stabilization in the phosphonium and sulfonium ylide cases (especially the latter) has to be attributed to the back-bonding stabilization involving the σ^* and/or 3d orbital participation. Discussion for elucidating this view is presented.

Introduction

Carbanions neighboring a positively charged substituent are referred to as "ylides" and are probably the best known synthons in modern synthetic chemistry due especially to their wide application in Wittig-type conversions.[1] Although presently the ylides most familiar to many people may still be the ones carrying triphenylphosphonium group (known as "Wittig reagents"), the past 2 to 3 decades have indeed witnessed a dramatic expansion of traditional ylide chemistry to include many other Group VB and VIB elements (such as N, As, Sb, S, Se, Te, etc.) both in their synthetic applications[2] and in detailed structural and mechanistic considerations.[3] As the new chemistry brought out by these new members of the ylide family continues to impart innovative impacts to many related areas, quantitative comparisons of their thermodynamic stabilities including all these major types of ylides have become more desirable because many previous investigations imply that the ylide reactivities, reaction paths, and stereochemistry are inherently stability-dependent.[1b,c,3f,g,k] A well-established way of measuring the thermodynamic stability of ylides is, of course,

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to examine the ease of the carbanion formation by removal of a proton from the carbon atom next to the onium ion. As known, the energetics of these processes are represented by their pK_a values. There are in fact many significant works on the equilibrium acidities of ylide conjugate acids in the early literature[4] which added a great deal to the current understanding of many aspects of ylide properties. However, because most previous pK_a measurements were done in different solvents, the direct comparisons of these data to obtain quantitative information on relative ylide stabilities are therefore practically not applicable. Indeed, Johnson[1c] has also noted this problem and stated that "measurement of the pK_a of an ylide conjugate acid has been a favorite technique to determine the influence of substituents, but *solvent variability has limited comparisons of the data*".

In the past 2 decades Bordwell and co-workers have established a so-called "absolute" acidity scale in dimethyl sulfoxide solution[5] which now includes nearly 2000 pK_a values and also finds many new applications in recent years.[6] In this solvent, equilibrium acidities of quite a few Ph_3P^+- and R_3N^+-containing ylide precursor salts were successfully determined.[7] However, except for one case (i.e., $Me_2S^+CH_3$[5]), onium salts other than the mentioned two types have virtually not been touched in the previous DMSO-phase acidity studies.[5a]

We have recently carried out some research work on the heterolytic and homolytic bond energies of certain theoretically interesting compounds utilizing the pK_a values in DMSO obtained in this laboratory.[8] A few families of arsonium and sulfonium ylide precursor salts were therein included.[8a,b] We found that the Ph_3As^+ salts are 2.5−5.1 pK units *less* acidic than the Ph_3P^+ salts of similar structure, whereas the R_2S^+ salts are 1.7−3.1 pK units *more* acidic than the corresponding R_3P^+ salts. These findings imply that the ylide stability order should be $R_2S^+{-}C^- > R_3P^+{-}C^- > R_3As^+{-}C^-$.

Chart 1

4-G-$C_6H_4CH_2P^+Ph_3Br^-$	4-G-$C_6H_4CH_2P^+Bu_3Br^-$	4-G-$C_6H_4CH_2P(O)Ph_2$
1	**2**	**3**
4-G-$C_6H_4CH_2As^+Ph_3Br^-$	4-G-$C_6H_4CH_2N^+Et_3Br^-$	4-G-$C_6H_4CH_2S^+Me_2Br^-$
4	**5**	**6**
4-G-$C_6H_4CH_2S^+Bu_2Br^-$	4-G-$C_6H_4CH_2Se^+Me_2Br^-$	4-G-$C_6H_4CH_2Se^+Bu_2Br^-$
7	**8**	**9**
4-G-$C_6H_4CH_2Te^+Bu_2Br^-$	9-E^+-FlHBr$^-$	$PhCOCH_2E^+Br^-$
10	**11**	**12**

G: a) H, b) CH_3, c) CF_3, d) CO_2Me, e) CN, f) NO_2, g) OMe

E^+: A) Ph_3P^+, B) Bu_3P^+, C) Ph_3As^+, D) Me_2S^+, E) Bu_2S^+, F) Me_2Se^+, G) Bu_2Te^+

However, the above experimentally observed stability order did not appear to be in line with what is predicted from the dipole polarizability parameters of the relevant center onium atoms [i.e., S (19.6) < P (24.5) < As (29.1)[9]], because the currently overwhelming view for the primary cause of an enhanced ylide stability is *polarization* rather than the previously believed resonance effect.[10] Therefore, the experimental results from our preliminary ylide stability study[8a,m] look very intriguing and certainly warrant further investigations.

In the present paper, we have extended our study on ylide thermodynamic stabilities to cover totally six different Group VB and VIB onium elements and many remotely substituted ylide derivatives. The structures of the related ylide precursor salts are shown in Chart 1 (**1**−**12**); among those, two families (**2**, **4**) have already appeared in the preliminary report.[8a] All the pK_a values of these ylide conjugate acids were determined *in a single solvent*, i.e., DMSO, which allows meaningful comparisons of thermodynamic stabilities for a comprehensive list of the Group VB and VIB ylides to be made on the basis of an "absolute" acidity scale. The bonding features of these ylides are accordingly presented and rationalized.

Results and Discussion

Effects of Onium Ions and Carbanion Structure. The DMSO acidity scale[5,11] developed mostly by Bordwell and co-workers constitutes a major body of the currently known pK_as in organic solvents[12] and is known to be

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Table 1. Equilibrium Acidities of $PhCH_2\text{-}E^+\cdot Br^-$, $PhC(O)CH_2\text{-}E^+\cdot Br^-$, and $9\text{-}E^+{-}FlH\cdot Br^-$ in DMSO at 25 °C

	$E^+\text{-}CH_2Ph$		$E^+\text{-}CH_2C(O)Ph$		$9\text{-}E^+\text{-}FlH$	
E^+	pK_a[a]	lit. pK_a[c]	pK_a[a]	lit. pK_a[c]	pK_a[a]	lit. pK_a[c]
H		43[d]		24.7[d]		22.6[d]
Me_3N^+		31.9[e]		14.6[e] 10.5 (80% EtOH)[h]		17.8[e]
Et_3N^+	30.8					
$Ph_2P(O)$	27.5					
Bu_2Te^+	23.8[b]		11.2		10.4	
Me_2Se^+	23.1		11.1			
Ph_3As^+	22.7[b]		8.6[b]	8.65 (80% EtOH)[h] 8.25 (95% EtOH)[i]	9.8[b]	7.8 (68% dioxane)[n]
Bu_3P^+	21.9[b]		10.1[b]	9.0 [j](80% EtOH)[h] 8.6[j](95% EtOH)[i]	10.7 [b]	8.0 (68% dioxane)[n] 10.5 (95% EtOH)[o]
Bu_2S^+	18.8_5		8.4			
Me_2S^+	17.8			8.45 (80% EtOH)[h] 7.68 (95% EtOH)[i]	6.5	7.3 (68% dioxane)[n] 13.7 (5% $DMSO_{aq}$)[p]
Ph_3P^+	17.6	17.4 [f] 12.6[g]		6.1 [f] 6.0 (80% EtOH)[h,k] 5.60 (95% EtOH)[i] 6.0 (MeOH)[l] 6.0 (H_2O)[m]		6.6 [f] 7.5 (68% dioxane)[n] 9.0 (95% EtOH)[o]

[a] Equilibrium acidities in DMSO at 25 °C measured in the present work by overlapping indicator methods[5a] (≥three-point titrations) except as otherwise specified. [b] Appeared in a preliminary report.[8a,m] [c] Literature pK_a values in DMSO except those specified in parentheses. [d] Reference 5a. [e] Reference 7a. [f] Reference 7b. [g] Sim, L. G.; Sale, K. D.; Utley, J. H. P. *J. Chem. Soc., Chem. Commun.* **1990**, 662. [h] Reference 4h. [i] Reference 4f. [j] Value for $Me_3P^+{-}CH_2C(O)Ph$. [k] Reference 4c. [l] Reference 4d. [m] Reference 4e. [n] Reference 4g. [o] Reference 4b. [p] Murray, C. J.; Jenks, W. P. *J. Am. Chem. Soc.* **1990**, *112*, 1880.

"intrinsic",[13] so it has served as a good quantitative guide in judging the thermodynamic stabilities of organic anions for a long time. Because a general comparison of ylide thermodynamic stabilities was intended in this work, we have carried out all the pK_a measurements for the ylide conjugate acids using DMSO as the sole solvent. The results are summarized in Tables 1 (for **11**, **12**, and **1a**−**9a**) and 2 (for **1**−**9**), together with the relevant DMSO phase pK_a data either from a preliminary work in this laboratory[8a,m] or from the work of Bordwell.[5a,7] The literature pK_as measured in other solvents (whichever available) are also listed for the purpose of comparison.

An examination of Table 1 shows that an α-N^+Et_3 substitution increases the stability of the adjacent benzylide carbanion by 12.2 pK units (16.6 kcal/mol, henceforth abbreviated as kcal), which is similar to the stabilizing effect of 11.1 pK by an α-N^+Me_3 reported by Bordwell.[7a] It is clear that although the Coulombic interaction of the α-N^+R_3 group with the neighboring carbanion is the greatest among the well-known strongly electron-withdrawing substituents such as R_3N^+, CN, and NO_2 [their field parameters (F) are 0.99, 0.51, and 0.65, respectively[14]], its acidifying effect was, nevertheless, found to be almost the weakest, compared to the remarkable 12.1 and 30.7 pK unit acid-strengthening effect for the latter two, respectively. This should be understandable because the R_3N^+ group shows a lack of resonance stabilization effect.[7] Not surprisingly, replacement of Et_3N^+ with a Ph_3As^+ group causes a further 8.1 pK unit (11.1 kcal) decrease in the corresponding pK_a, suggesting that either the polarization of the arsonium cation or the resonance utilizing its 4d orbitals, or both, may play an important role in stabilizing the adjacent carbanion. It is well realized, however, that the once believed concept of the (p−d)π resonance stabilization in phosphonium ylide[10] has been widely challenged in recent years, mostly from theoretical points of view.[15] The overwhelming discussions in the recent literature thus tend to discount the importance of resonance contribution from canonical formula **Ib** to the enhanced ylide stability and are much

$$\underset{\textbf{Ia}}{P^+\text{-}C^-} \quad \leftrightarrow \quad \underset{\textbf{Ib}}{P{=}C}$$

in favor of a joint contribution of Coulombic interaction and polarization between the onium ion and adjacent carbanion to ylide stability.[17] As for the present Ph_3As^+ case, the 11 kcal increase in the stability of $PhCH^-As^+Ph_3$ as compared to $PhCH^-N^+Et_3$ may be similarly rationalized, based on the polarization argument, because the polarizability of As is indeed much greater than that of N as judged by their dipole polarizability parameters (29.1 versus 7.4[9]). However, the rationale for the 7 kcal greater stability of $Ph_3P^+CH^-Ph$ (pK_a = 17.6) as compared to that of the $Ph_3As^+{-}CH^-Ph$ (pK_a = 22.7) is not that straightforward, if only the polarization and Coulombic effects are taken into account, because the polarization and inductive effects for P are both smaller than those of the As atom (polarization parameters are 24.5 versus 29.1,[9] the field parameter σ_Fs are 0.97 versus 1.05[14]). Obviously, the observed stability order can only be understood if all the components of electronic effects including a contribution from resonance effect are invoked in consideration, because the 3d orbitals of the P atom and the P−C σ^* bond are known to be much more

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efficient in interacting with the neighboring negative charge in the carbon 2p orbital than the 4d orbitals of As and the As−C σ^* bond.[3c,g] The order of $Ph_3P^+ > Ph_3As^+ > Me_3N^+$(or Et_3N^+) in stabilizing the adjacent benzylide anion observed in the present work [the DMSO phase pK_as are 17.6, 22.7, and 31.9 (or 30.8), respectively] is in fact consistent with the pK_a order of $6.0 < 8.65 < 10.5$ for the same onium ions attaching to the phenacyl anion (the so-called stabilized ylide) in 80% EtOH,[4h] although the effect in the latter case was very much masked by solvent leveling.

The stability of the Group VIB ylides can be viewed in a similar manner. The pK_as of 17.8 for $Me_2S^+CH_2Ph$ and 18.8_5 for $Bu_2S^+CH_2Ph$ (Table 1) indicate that the sulfonium ylide is the most stable one among the series of $R_2S^+{-}C^-$, $R_2Se^+{-}C^-$, and $R_2Te^+{-}C^-$ by a margin of about 7 kcal (∼5 pK units) compared to the other two members (the pK_as for $Me_2Se^+CH_2Ph$ and $Bu_2Te^+CH_2Ph$ are 23.1 and 23.8, respectively). The same trend was seen in the phenacyl series as well by comparison of their respective pK_as of 8.4, 11.1, and 11.2 (Table 1), although the margins here get smaller due to a more effective charge delocalization by the carbonyl group (i.e., a saturation effect). It is realized here again that the observed greater stability of the sulfur ylides cannot be fully accounted for, if only the polarization and field effects are considered, because the comparisons of these two mentioned effects for S, Se, and Te atoms would just indicate an opposite trend due to the fact that their polarizability increases in the order 19.6 (S) < 25.4 (Se) < ∼35 (Te)[9,18] and their field/inductive effect is about of the same size.[14] This order of thermodynamic stability could be understood, nevertheless, by considering the resonance contribution resulting from the characteristic bonding situation of the sulfur ylide. It is conceivable that the shorter S−C bond as compared to the P−C bond[3f,17] would certainly enhance the chance for the sulfur 3d orbitals [in the form of (p−d)π bonding] and the (S−C)* bond (in the form of back-bonding) to have a much stronger interaction with the ylidic carbanion than those in the phosphorus ylide. Although the idea for the contribution from d orbitals to ylide stability has been severely questioned in the literature,[15,16] arguments in support of the resonance- and back-bonding-based stabilization have in fact never ceased and are especially favored from the point of view of inorganic chemists.[3d,19] A recent ESR study on the $(Ph_3P\overset{\cdot\cdot}{-}CH\overset{\cdot\cdot}{-}CR_2)^{\bullet}$ radical indicates that spin delocalization into the phosphorus 3d orbitals should indeed not be neglected.[20] Therefore, the partial stabilization resulted from spin-delocalization to the better-reaching 3d orbitals of sulfur atom would be expected to be greater.

As for the cases where the stabilities of $Te^+{-}$ and $Se^+{-}$ylides are considered, the Te−C and Se−C bonds are probably too far-reaching for a reasonable back-bonding interaction to be functionable, so the polarization effect may come to play a more important role in ylide stability. In these cases, the gained stabilization from a stronger Coulombic interaction in the $Se^+{-}$ylide due to its shorter bond (relative to the Te−C bond) may be offset by its weaker polarizability as compared to that of the Te atom in $Te^+{-}$ylide. As indicated by their comparable pK_a values, this is apparently the case. The lack of a back-bonding stabilization in the $Se^+{-}$ and $Te^+{-}$ylides also explains why their pK_as are both higher than that of the sulfur ylide in the same family.

It is also of interest to compare the stabilities of the Group VB and VIB ylides in the same row (i.e., same period). There are two such pairs in Table 1, i.e., $P^+{-}C^-/S^+{-}C^-$ and $As^+{-}C^-/Se^+{-}C^-$. From the pK_as of 21.9 for $Bu_3P^+CH_2Ph$ versus 18.8_5 for $Bu_2S^+CH_2Ph$, 10.1 for $Bu_3P^+CH_2COPh$ versus 8.4 for $Bu_2S^+CH_2COPh$, and 10.7 for 9-Bu_3P^+FlH versus 6.5 for 9-Me_2S^+FlH, it is obvious that the sulfur ylide is thermodynamically more stable than the phosphorus ylide if the substituent on the onium ion is kept the same or about the same. A similar trend can be seen in other solvents too, upon comparing the pK_as of 9.0 for $Bu_3P^+CH_2COPh$ versus 8.4_5 for Me_2S^+-CH_2COPh in 80% EtOH[4h] and the pK_as of 8.0 for 9-Bu_3P^+-FlH versus 7.3 for 9-Me_2S^+FlH in 31.7 H_2O−68.3 dioxane,[4g] although the differences in the pK_as in these aqueous solvents are much smaller. While the reasons for the observed stability order may not be simple and certainly deserve further theoretical considerations, we tend again here to relate the greater stability of the sulfur ylide to its stronger back-bonding and (p−d)π bonding stabilization due to the shorter $S^+{-}C^-$ bond. This is because the dipole polarizability parameters of 19.6 for S versus 24.5 for P[9] and the comparable size of their field effects (the F constants are 0.98 and 0.94 for Me_2S^+ and Et_3P^+, respectively[14]) would point to an opposite order[21] if the back-bonding effects were not counted. In the case where the arsonium and selenonium ylides are compared, the pK_as of 22.7 for $Ph_3As^+CH_2Ph$ versus 23.1 for Me_2Se^+-CH_2Ph and 8.6 for $Ph_3As^+CH_2COPh$ versus 11.1 for $Me_2Se^+CH_2COPh$ seem to indicate that the former ylide is thermodynamically more stable. It is noted, however, that the substituents on the onium ions in the cases compared are actually not the same, therefore if the phenyl group in Ph_3As^+ is replaced by an alkyl group, the pK_a may very well be higher than that of the $R_2Se^+{-}$ylide being compared because replacing phenyl groups in $Ph_3P^+{-}$ylides with n-butyl resulted in an increase in the pK_a by at least 4 units (Table 1). If this is also true for arsonium ylides (note that As−ylides are less stable than P−ylides and therefore should be more sensitive to structural changes), the presumably lower pK_a of $R_2Se^+{-}$ylide relative to that of $R_2As^+{-}$ylide would then just show a similar pattern of the relative ylide stability and could be similarly explained.

The effect of onium ions on ylide stability is found to be influenced also by the structural feature on the side of the carbanion. Bordwell has observed that replacing a hydrogen atom at the methylene carbon with Me_3N^+ in toluene, acetophenone, and fluorene strengthened their acidity by 11.1, 10.1, and 4.8 pK units, respectively.[7a] The

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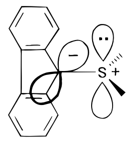
(18) The dipole polarizability of ∼35 for Te is a rough estimate based on comparisons with the relevant values listed in ref 9.

(19) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988. (b) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, 1984. (c) Angyan, J. G.; Poirier, P. A.; Kucsman, A.; Csizmedia, I. G. *J. Am. Chem. Soc.* **1987**, *109*, 2237. (d) Maouche, Y.; Brianso, M. C.; Maouche, B. *THEOCHEM* **1988**, *166*, 449.

(20) Geoffroy, M.; Rao, G.; Tancic, Z.; Bernardinelli, G. *J. Am. Chem. Soc.* **1990**, *112*, 2826.

(21) It is well-known that the order of ylide thermodynamic stability may not always parallel to the order of ylide reactivity because the latter may not be affected entirely by the ylide nucleophilicity. For example, while both experimental observation and calculation indicate that the order of their Wittig reactivity is $P^+{-}C^- > S^+{-}C^-$, which does agree to the order of their thermodynamic stability observed in this work, the order of their Corey−Chaykovsky reactivity showed, however, an opposite order.[3f,22]

acidity order for the latter two onium salts was reversed (14.6 versus 17.8) in reference to the pK_as of their parents (24.7 versus 22.6) due to steric inhibition of solvation of the Me_3N^+-bearing fluorenide ion.[7a] An acidity reversal was also observed with an α-Ph_3P^+ substitution (Table 1),[7b] although the pK_a difference is diminished due partially to the insensitivity of the polarization effect of Ph_3P^+ to steric variation. In the present work, a similar situation is found when the onium ion is Ph_3As^+ or Bu_3P^+. However, there are also two cases ($E^+ = Bu_2Te^+$, R_2S^+) where the acidity order of the E^+-substituted species was found to parallel that of their parents, indicating the absence of a solvation differentiation. For the Bu_2Te^+ case, this could be understood by thinking that Te is the only fifth period element in Table 1 so the Te−C bond is probably long enough to depress the effect of a possible steric inhibition of solvation by the Bu_2Te^+ group. Whereas in the R_2S^+ case, both X-ray analysis[16a] and MO calculation[3f,16b] indicate that the two methyl groups in $Me_2S^+{-}C^-$ would be aligned in a plane perpendicular to the fluorenyl ring due to a four-electron repulsion (see formulas **II**), therefore the acidifying effect of Me_2S^+ by either back-bonding or a partial (p−d)π overlapping (see text above) will be maximized and, in the meantime, the effect of steric inhibition of solvation will be minimized, thus leading to a "normal" acidity order for $Bu_2S^+{-}CH_2COPh$ versus 9-Me_2S^+−FlH.



II

The pK_as determined previously in other solvents[4] for the ylide conjugate acids of interest in the present work are collected in Table 1, whenever available. A general inspection of the data shows that most pK_as in various hydroxylic solvents are much lower than those in DMSO measured in the present work except for a few Ph_3P^+-substituted delocalized ylides. The lower pK_a in hydroxylic solvents is generally observed for neutral acids as well[5] and is caused by the greater hydrogen bonding stabilization of the anions in those solvents. The extent of hydrogen bonding is different for various hydroxylic solvents; therefore the reported pK_as of the same compounds obtained in different media[4] do not generally agree with each other.

Effects of Remote Substituents on Carbanion. Compared to the structural effects on onium cations, there is more work on the stabilities of ylidic carbanions as judged by their pK_a variation. As showed in the literature, the previous center of focus was mainly on various phosphonium ylides.[4,7b] Recently, a thorough study on the effects of adjacent substituents on the equilibrium acidities of trimethylammonium and pyridinium ylide precursors in DMSO was also reported.[7a] A comprehensive comparison of the effects of remote substituents for different types of ylides is essentially absent, however. The present work thus partially aimed to compare the remote substituent effects on the stabilities of various Group VB and VIB onium-substituted benzylide ions. The pK_as of the compounds suitable for this purpose are listed in Table 2. To reveal the effects of remote substituents and of the onium ions on ylide stabilities, a Hammette-type correlation analysis of pK_a values of various E^+-CH_2Ar families versus the corresponding σ_p^- constants was carried out. The results are summarized in Table 3.

Table 2. Equilibrium Acidities of Conjugate Acids of $ArCH^-$-E^+ Ylides in DMSO at 25 °C

	pK_a in DMSO[a]						
E^+	H	CH_3	CF_3	CO_2Me	CN	NO_2	MeO
Ph_3P^+ (**1**)	17.6	18.0	14.6	14.2	13.3_5	11.4[c]	
$Ph_2P^+{-}O^-$ (**3**)	27.5	28.0	23.6				29.2
Et_3N^+ (**5**)	30.8			27.6	27.1		
Me_2S^+ (**6**)	17.8	18.4		14.5	14.6	13.6[c]	
Bu_2S^+ (**7**)	18.8_5						
Me_2Se^+ (**8**)	23.1	23.6[b]	19.5	19.2			
Bu_2Se^+ (**9**)	23.5[b]						
Bu_2Te^+ (**10**)	23.8[b]	24.2	19.6	18.7	18.5	16.4[c]	

[a] Equilibrium acidities in DMSO at 25 °C measured in the present work by overlapping indicator methods[5a] (≥three-point titrations) except as otherwise specified. [b] Average value of repeated one-point titration due to instability of the anion. [c] Measured by the "double-standard-acid method" of this laboratory (see Experimental Section).

Table 3. Correlation Analysis of Equilibrium Acidities of E^+-$CH_2C_6H_4$-G-*p* versus σ_p^- Constants[a]

	E^+-$CH_2C_6H_4$-G-*p* pK_a(G) = $\rho\sigma_p^-$(G) + *a*		
E^+	*r*	ρ	*a*
Et_3N^+	0.993	−3.83	30.7
Ph_3P^+	0.994	−4.46	17.5
Bu_3P^+	0.995	−5.00	22.1
$Ph_2P(O)$	0.993	−5.86	27.4
Ph_3As^+	0.989	−5.35	22.6
Me_2S^+	0.989	−3.40	17.7
Me_2Se^+	0.997	−5.03	22.9
Bu_2Te^+	0.991	−5.50	23.4

[a] The pK_as used in correlation are DMSO-phase values from Table 2. The σ_p^- constants are from ref 14.

It is not unexpected to see from Table 3 that the pK_as linearly correlate with σ_p^- constants reasonably well for all the remotely substituted E^+-CH_2Ar families, because both pK_a and σ_p^- are good models for carbanion stability as affected by remote substitution. An inspection on the ρ values of these linear correlations further indicates that the sensitivity of the pK_as to the changes of *para* substituents varies quite substantially with structural variations of the onium ions, ranging from −5.86 as the most sensitive [for $E^+ = Ph_2P(O)$] down to −3.4 as the least sensitive (for $E^+ = Me_2S^+$). It is well-known that a larger ρ value is related to a higher charge localization at the carbanion center, and vice versa, so the electron density on the benzylic carbon next to the Ph_3P^+ group must be lower than that in the Ph_3As^+-substituted benzylide anion (i.e., $Ph_3As^+CH^-Ar$) according to their respective ρ values of −4.46 and −5.35. Similarly, the degree of charge localization on carbanions of the Group VIB ylide series and of the phosphonium ylides, as judged by the ρ parameters, is shown to be in the following decreasing order: Bu_2Te^+ (−5.50) > Me_2Se^+ (−5.03) > Me_2S^+ (−3.40) and $Ph_2P(O)$ (−5.86) > *n*-Bu_3P^+ (−5.00) > Ph_3P^+ (−4.46), respectively. Similar to the argument discussed in a previous section invoking the back-bonding stabilization and/or a partial (p−d)π interaction for rationalizing the greater ylidic carbanion stability observed for the third-row onium-bearing ylides (e.g., $Ph_3P^+{-}C^-$ and $Me_2S^+{-}C^-$), here again the lower charge density on the benzylic carbons of Ph_3P^+−ylide (relative to Ph_3As^+−ylide) and of Me_2S^+−ylide (relative to R_2Se^+− and R_2Te^+−ylides), as judged by their respective ρ values, can be explained by the same structural rationale.[23] The situation for the phosphonium subgroup is somewhat different, however. It is most likely that the relative ease of polarization would be more responsible for the greater charge dispersion in the Ph_3P^+ case than in the n-Bu_3P^+ case. The $Ph_2P(O)$-substituted series shows the largest sensitivity simply because it is in fact the weakest electron-pulling group among those under comparison; thus the negative charge on its neighboring carbon should be the most localized among this series.

Summary and Conclusion

On the basis of the comparisons of about 50 DMSO-phase pK_as of the substituted Group VB and VIB ylide families, it can be concluded that (i) all the onium ion substituents are strongly ylide-stabilizing by virtue either of their electrostatic abstraction and polarization abilities or of the abilities in resonance delocalization, (ii) the substantially weaker acidifying effect of the Ph_3As^+ group (which is even more polarizable than Ph_3P^+ and has a comparable size of electrostatic interaction with the adjacent carbanion as that for the Ph_3P^+ group) as compared to Ph_3P^+ ($\Delta pK = 5.1$, or ~7 kcal for E^+-substituted toluene) suggests that an involvement of the (p−d)π and/or back-bonding stabilization must be at least partially responsible for the higher thermodynamic stability of the Ph_3P^+−ylides, (iii) the greater ylide-stabilizing effect of the less polarizable R_2S^+ group (see ref 9 and text for data) as compared to that of the n-Bu_2Se^+ and n-Bu_2Te^+ groups and to that of the n-Bu_3P^+ group, as shown by their respective ΔpK_as of ~5 (~7 kcal) and ~3 (4.7 kcal), can be viewd as another indication for the involvement of the (p−d)π bonding and/or the (S−C) σ^* back-bonding in stabilizing the adjacent carbanion, (iv) a good to excellent linear correlation of the pK_as versus the σ^- constants was observed for all the remotely substituted E^+-CH_2Ar families (Table 3), which indicates that the extent of charge dispersion on carbanions, as registered by the slopes (ρ) of these correlation lines, corresponds well to the relative abilities of the onium ions in utilizing their d and σ^* orbitals to stabilize the benzylide anions, (v) due to the four-electron repulsion in sulfonium ylide (formulas **II**), the anion-stabilizing ability of Me_2S^+ in $Me_2S^+-Fl^-$ is enhanced upon a beneficial avoidance of a possible steric congestion and thus overshadows the steric inhibition of solvation effect seen in other E^+-Fl^- systems and explains the "normalized" acidity order observed in the present work, and, finally, (vi) the unified solvent system (DMSO) for all the pK_as studied in this work allows a meaningful comparison on the ylide thermodynamic stabilities to be made as shown (if substituents on the onium ion are similar): for Group VB, $P^+-C^- > As^+-C^- > N^+-C^-$; for Group VIB, $S^+-C^- > Se^+-C^- -Te^+-C^-$; and for third-row elements, $S^+-C^- > P^+-C^-$.

Table 4. Equilibrium Acidities of Onium Salts in Dimethyl Sulfoxide at 25 °C

substr	pK_a^{a}	indicator (pK_{InH})	no. of runs	assigned pK_a
1a	17.58 ± 0.00	PFH^c (17.9)	2	17.6
1b	18.04 ± 0.04	CNAN^d (18.9)	2	18.0
1c	14.63 ± 0.02	HZF^e (14.95)	2	14.6
1d	14.19 ± 0.01	HZFP2^f (14.15)	2	14.2
1e	13.35 ± 0.03	HZFP2^f (14.15)	3	13.3_5
1f	11.43 ± 0.04	NBY300^{g,h} (12.25)	2	11.4
3a	27.54 ± 0.19	PXH^i (27.9)	3	27.5
3g	29.22 ± 0.02	PXH^i (27.9)	2	29.2
3b	28.03 ± 0.01	PXH^i (27.9)	2	28.0
3c	23.56 ± 0.02	FH^j (22.6)	2	23.6
5a	30.77 ± 0.10	TH^k (30.6)	2	30.8
5d	27.61 ± 0.02	PXH^i (27.9)	2	27.6
5e	27.10 ± 0.11	PXH^i (27.9)	3	27.1
6a	17.79 ± 0.04	CNAH^d (18.9)	3	17.8
6b	18.38 ± 0.05	PFH^c (17.9)	2	18.4
6d	14.60 ± 0.03	HZFO2^l (12.95)	2	14.6
6e	14.54 ± 0.07	HZFO2^l (12.95)	2	14.5
6f	13.57 ± 0.12	NBY300^h (12.25)	3	13.6
7	18.85 ± 0.05	CNAH^d (18.9)	2	18.8_5
8a	23.13 ± 0.07	FH^j (22.6)	3	23.1
8b	23.61 ± 0.05	FH^{j,m} (22.6)	4	23.6
8c	19.52 ± 0.10	CNAH^d (18.9)	3	19.5
8d	19.17 ± 0.06	CNAH^d (18.9)	3	19.2
9	23.5 ± 0.10	FH^j (22.6)	3	23.5
10a	23.80 ± 0.13^b	TBUFH^n (24.35)	3	23.8
10b	24.20 ± 0.13	TBUFH^n (24.35)	2	24.2
10c	19.64 ± 0.13	CNAH^d (18.9)	2	19.6
10d	18.69 ± 0.13	CNAH^d (18.9)	3	18.7
10e	18.49 ± 0.16	CNAH^d (18.9)	2	18.5
10f	16.4 ± 0.2	JIY300^o (15.0)	3	16.4
11B	10.66 ± 0.10	9COMFH^p (10.35)	2	10.7
11C	9.77 ± 0.11	9COMFH^p (10.35)	3	9.8
11D	6.52 ± 0.07	F279CO^q (6.5)	2	6.5
11G	10.40 ± 0.01	9COMFH^p (10.35)	2	10.4
12B	10.08 ± 0.13	9COMFH^p (10.35)	2	10.1
12C	8.56 ± 0.02	9CNFH^r (8.3)	2	8.6
12E	8.41 ± 0.03	9CNFH^r(8.3)	2	8.4
12F	11.07 ± 0.02	9COMFH^p(10.35)	2	11.1
12G	11.21 ± 0.02	9COMFH^p(10.35)	2	11.2

[a] Equilibrium acidities measured in DMSO at 25 °C. [b] Reference 30. [c] 9-Phenylfluorene. [d] 4-Chloro-2-nitroaniline. [e] 9-Fluorenone -phenylhydrazone. [f] 9-Fluorenone(4-chlorophenyl)hydrazone. [g] Diphenylsulfonylmethane. [h] Measured by the "double-dtandard-dcid (DSA)" method. First SA: (m-chlorobenzyl)phenyl sulfone. Second SA: diphenylsulfonylmethane (NBY300). [i] 9-Phenylxanthene. [j] Fluorene. [k] Triphenylmethane. [l] 9-Fluorenone (2-chlorophenyl)hydrazone. [m] One-point titration. [n] 9-*tert*-Butylfluorene. [o] Measured by DSA method. First SA: dibenzyl sulfone. Second SA: JIY 300. [p] (9-Methoxycarbonyl)fluorene. [q] 2,7-Dibromo-9-(methoxycarbonyl)fluorene. [r] 9-Cyanofluorene.

Experimental Section

Melting points are uncorrected. The ^1H NMR spectra of the onium salts were recorded at 90 MHz with tetramethylsilane (TMS) as internal standard. Reagents and solvents used in synthesis were purified according to standard procedures; their purity was confirmed by melting points (solid samples), NMR, or GC analysis.

Materials. The indicators and standard acids used in the pK_a measurement were either prepared in this lab by the methods described in the literature[5a] or gifts from Prof. E. M. Arnett of Duke University, except for those which were commerically available. P-(4-Substituted benzyl)triphenylphosphonium bromides (**1**),[24] P-(4-substituted benzyl)diphenylphosphine oxides (**3**),[25,26] N-(4-substituted benzyl)triethylammoni-

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[22] (a) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1962**, *84*, 867. (b) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353. (c) Johnson, A. W.; Lacount, R. B. *J. Am. Chem. Soc.* **1961**, *83*, 417.

[23] A discussion on the Et_3N^+-substituted series was not intended here because it is not structurally comparable with all others for not having functionable d-orbitals and the points in correlation are also too limited ($n = 3$) for the correlation data to be highly reliable.

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[26] Mesyats, S. P.; Tsvetkov, E. N.; Petrov, E. S.; Shelganova, N. N.; Shcherbina, T. M.; Schatenshtein, A. I.; Kabachnilz, M. I. *Iza. Akad. Nauk SSSR, Ser, Khim.* **1974**, *11*, 2497.

um bromides (**5**),[27] *S*-(4-substituted benzyl)dimethylsulfonium bromides (**6**),[27] *S*-benzyldi-(*n*-butyl)sulfonium bromides (**7**),[27] *Se*-(4-substituted benzyl)dimethylselenonium bromides (**8**),[27] *Se*-benzyldi(*n*-butyl)selenonium bromide (**9**),[27] *Te*-(4-substituted benzyl)di(*n*-butyl)telluronium bromides (**10**),[27] *P*-flourenyltri(*n*-butyl)phosphonium bromide (**11B**),[28] *As*-fluorenyltriphenylarsonium bromide (**11C**),[28] *S*-fluorenyldimethylsulfonium bromide (**11D**),[28] *Se*-fluorenyldimethylselenonium bromide (**11F**),[28] *Te*-fluorenyldi(*n*-butyl)telluronium bromide (**11G**),[28] and the bromide salts[28] of *P*-phenacyltri(*n*-butyl)phosphonium (**12B**), *As*-phenacyltriphenylarsonium (**12C**), *S*-phenacyldi(*n*-butyl)sulfonium (**12E**), *Se*-phenacyldimethylselenonium (**12F**), and *Te*-phenacyldi(*n*-butyl)telluronium (**12G**) were generally prepared by literature methods or by modified literature procedures. All purified products gave NMR spectra in agreement with the assigned structures. For onium salts which appeared to be new, elemental analyses were performed and were shown to agree with the corresponding theoretical values of the assigned structures. Comparisons of the melting points for the rest with the known literature data were also found to be satisfactory. Their melting points, ^{1}H NMR data, recrystallization solvents, and elemental analyses (for new compounds) are provided in the Supporting Information.

Equilibrium Acidity (pK_a) Measurement. The DMSO-phase equilibrium acidities of the onium salts listed in Tables 1 and 2 were determined at 25 °C on a UV/vis spectrophotometer by the "overlapping indicator method" described in the literature[5a] (excepted for the ones specified below) under vigorous oxygen-free and water-free conditions. Purification of the solvent and preperation of the potassium dimsyl base ($CH_3SOCH_2^-K^+$) solution were carried out following the authetic procedure in ref 29. All the ylide carbanions were stable enough to allow a pK_a value to be evaluated on the basis of at least three consecutive titrations, except for the cases of R_2-Se^+CH_2Ph (**8b** and **9**) where only one quick titration was possible due to the instability of the system. For determination of the pK_as for compounds **1f**, **6f**, and **10f**, a so-called "Double-Standard-Acid" (DSA) method,[8f] which is a modified version of the "overlapping indicator method" of Bordwell by using two nonabsorptive standard acids of known pK_as instead of using only one indicator as in the normal case, was developed to derive the data. The first standard acid whose pK_a is chosen to be much lower than that of the solvent (DMSO) but at least 3 pK higher than that of the substrate of interest was used to deprotonate the onium salt. After a good Beer's law plot was obtained, the second standard acid whose pK_a should be within close vicinity of that of the substrate ($\Delta pK_a < 1.5$) was titrated in to establish an equilibrium system. The UV absorption change of the substrate anion upon titration was recorded; then a combination of the equilibrium absorption with the information on initial concentrations allowed the desired pK_a to be evaluated by simple computer progressing. This method was originally developed for pK_a measurement of some compounds whose secondary deprotonation may be affected by a superbase like dimsyl, but it may also be applicable to systems sensitive to strong basic conditions. The pK_a values measured by both methods, together with the indicators or the standard acids used, are summarized in Table 4.

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Supporting Information Available: Spectroscopic data (^{1}H NMR), melting points, recrystallization solvents, and elemental analyses for compounds listed in Tables 1 and 2; plots of linear correaltion for the regression equations shown in Table 3 (9 pages). See any current masthead page for ordering and Internet access information.

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(30) Anions in this series are less stable. Therefore a quick three-point titration was made and the titration manner was followed as close to each other as possible in order to minimize the systematic error within the family. Larger standard deviation is still obvious as the result of the low anion stability.