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AN ELECTRONEGATIVITY MODEL FOR POLAR GROUND-STATE EFFECTS ON BOND DISSOCIATION ENERGIES

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Homolytic bond dissociation energies are a composite of the radical stabilization energies (*RSE*) of the product radicals and the polar ground-state stabilization energies (*PSE*) of the reactant molecules. Substituent effects on the *PSE* are rationalized in terms of changes in the difference of group electronegativities. Thus, the PSE is composed of a bond polarity term, which measures the contribution due to the change in the electronegativity difference between the atoms in the bond, which is broken, and a polar relaxation term, which accounts for the substituent-dependent group electronegativity changes in the remaining bonds. A semi-quantitative model based on Pauling's bonding theory is suitable to assess the direction and relative magnitude of such effects. For the cleavage of benzylic and related bonds, the polar relaxation energy can be neglected (one-bond approximation) to allow the use of correlation analyses and substituent σ parameters for the interpretation of aryl substituent effects on the *PSE*. Accordingly, the plots of the *PSE*s *versus* σ substituent parameters should be linear, curved or parabolic depending on the electronegativity difference of the atoms in the bond being broken (Δ*EN*); moreover, the slopes (ρ values) should increase linearly with Δ*EN*. The predicted dependences of the *PSE*s on aryl substituents are compared with known experimental results and with the data obtained from semiempirical calculations. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

A principal challenge in mechanistic radical chemistry is the characterization of substituent effects on the bond dissociation energy (*BDE*), since their measurement provides information on the radical stabilization energy (*RSE*).[1] In organic chemistry [equation (1)], where one is dealing with an organic radical ($XR^{\bullet}$) and another fragment ($Z^{\bullet}$),

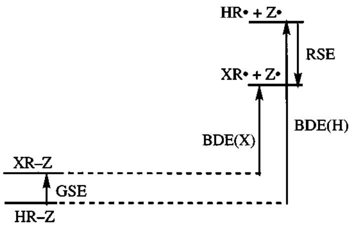
$$XR{-}Z \rightarrow XR^{\bullet} + Z^{\bullet} \qquad (1)$$

$$XR = XCH_2,\ XC_6H_4CH_2,\ XC_6H_4O,\ XC_6H_4NH, \text{ etc.}$$

$$\Delta BDE = RSE - GSE \qquad (2)$$

substituent effects on the RSE can be evaluated by comparison of the *BDE* for a substituted molecule XR—Z relative to the unsubstituted case, HR—Z.[1–3] Since the fragment Z is not varied for the examination of the effects of the substituent X (Scheme 1), the difference in *BDE* is a function of the *RSE* of X and the ground-state stabilization energy (*GSE*), which measures the effect of X on the intact molecule [equation (2)].[4, 5] The accurate knowledge of the latter presents a major limitation for the determination of *RSE*s from the experimentally accessible *BDE*s.[4, 5]

Steric restraints are well known to affect the ground-state energies of molecules.[2, 3, 6–8] However, steric effects by remote substituents[8–28] should be negligible, e.g. for the homolysis of benzylic and related bonds like those in structures **1**–**6**. Hence the simplifying assumption has been made that the influence of the substituents on the *GSE* should be minor compared with their effects on the *RSE*, i.e. $GSE \ll RSE$ and $\Delta BDE \approx RSE$. Examples include studies on the *BDE*s of phenylacetonitriles **1**,[18, 19] phenols **2**,[11] anilines **3**[20] and fluorenes **4**.[18, 21] Similarly, the homolysis rate constants of the arylcyclopropanes **5**[22–25] and phenylazoalkanes **6**,[26–28] which are assumed to be a function of the



Scheme 1

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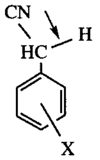

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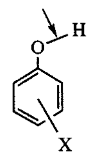

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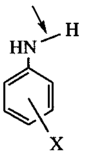

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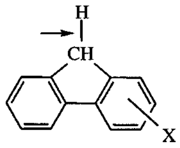

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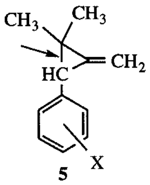

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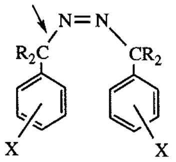

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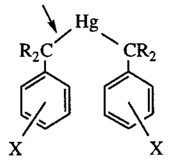

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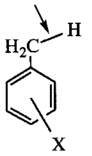

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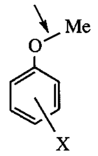

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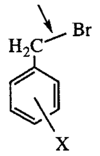

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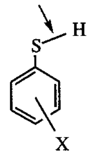

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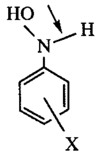

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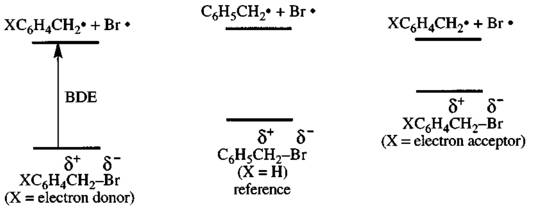
*BDE*s, have been directly interpreted in terms of radical-stabilizing substituent effects, while ground-state effects were not considered.

The assumed absence of ground-state effects of aryl substituents on the *BDE*s of benzylic and related bonds has been brought into question, in particular for the aryl derivatives **7**–**12**. Here, ground-state effects of aryl substituents on the *BDE*s were considered to be significant in comparison with the effects on the *RSE*.[29–46] The nature of these substituent effects on benzylic and related bonds is thought to be polar in nature, in keeping with Nicholas and Arnold's earlier postulate that polar substituent effects become important whenever the bond to be homolytically broken exhibits a net dipole moment.[47] Thus, the ground-state stabilization energy (*GSE*) must generally be expressed [equation (3)] as a composite of a *steric* ground state (de)stabilization energy (*SSE*) and a *polar* ground-state stabilization energy (*PSE*). Consequently, ground-state contributions to the *BDE* may become important even in the absence of steric effects, when polar ground-state effects are sizable, i.e. $SSE \approx 0$ and $GSE = PSE$ [equation (4)].

$$GSE = SSE + PSE \tag{3}$$

$$\Delta BDE = RSE - PSE \quad \text{for } SSE \approx 0 \tag{4}$$

Polar ground-state effects have been invoked by Jackson and co-workers for the homolysis of the dibenzylmercury compounds **7**;[30–33] here, the $Hg^{\delta+}$—$^{\delta-}CH_2Ar$ bond was thought to be stabilized by electron-accepting aryl substituents, which are capable of delocalizing part of the negative benzylic charge. The variations of the *BDE*s of the aryl-substituted toluenes **8**[44–46] and anisoles **9**[34] were also in part attributed to polar ground-state effects, the importance of which has also been emphasized by Clark and Wayner.[35] The latter authors have measured the *BDE*s of the benzyl bromides **10** and observed a linear correlation with Hammett's σ values. The negative ρ constant was interpreted in terms of a stabilization of the positive benzylic charge in the $Br^{\delta-}$—$^{\delta+}CH_2Ar$ bond by electron donors, which would thereby strengthen the bond and increase the *BDE* (Scheme 2).



Scheme 2

Further experimental evidence for the contribution of polar ground-state effects to the *BDE*s was presented by Bordwell and co-workers.[37–40, 48, 49] While new experimental data were reported for the thiophenols **11** and phenylhydroxylamines **12**, the previous experimental BDEs of the aryl derivatives **1**–**4** were also reinterpreted, following the suggestion of Clark and Wayner,[35] in terms of ground-state effects.[37] We have recently re-examined the thermolysis rates for various derivatives of the azoalkanes **7**,[26–28, 33, 41] which are thought to be a measure of the *BDE*s in these molecules. Two-parameter Hammett analyses revealed again polar ground-state effects on the benzylic bond, polarized according to $N{=}N^{\delta-}$—$^{\delta+}CR_2Ar$, where electron donors would lower the ground-state energy analogous to the situation in benzyl bromides (Scheme 2), and thereby increase the *BDE* or lower the relative thermolysis rates. In addition to the experimental efforts, quantum-mechanical calculations have been employed to obtain information on the substituent effects on the *BDE*[50—52] and to separate polar ground-state from radical effects.[29,34,41,42,53]

The recent growing awareness of polar ground-state contributions to the *BDE*s of benzylic and related bonds warrants a more detailed understanding of their origin and methods for the assessment of the relevant *PSE*s. Interestingly, while the polar effects of aryl substituents have been rationalized (e.g. Scheme 2), the available qualitative explanations are intuitive with respect to their origin.[32, 35, 37, 42] Clearly, what is missing is a conceptual link to a quantitative treatment of *BDE*s to allow *a priori* predictions of the expected magnitude and direction of the effects.

As an extension of our recent computational study,[53] the scope of Pauling's original bonding and electronegativity theory[54] for the interpretation of polar ground-state effects is now further evaluated. Simple electronegativity arguments have often been employed to rationalize trends in homolytic *BDE*s or organic molecules,[47, 55–62] or to explain trends in the activation energies and kinetics of radical reactions.[63, 64] However, previous discussions have focused on aliphatic systems, where steric ground-state effects of the substituents X will always interfere with polar ground state effects [equation (3)] and, thus, complicate the separation of the latter.[3, 8, 47, 55, 56, 64] Moreover, since electronegativity arguments have not been preferred in the pertinent recent studies on the *BDE*s of benzylic bonds,[29–43] the present finding, that the changes in *PSE*s can be directly related to the changes in the electronegativity difference between the atoms in the benzylic bond, and can be appropriately evaluated by linear energy relationships, should be of interest. The present rationalization for polar ground-state effects allows one to treat experimental data in a semi-quantitative manner, and to express, by means of calculations, *a priori* expectations on the presence and magnitude of the effects.

RESULTS AND DISCUSSION

Origin of polar ground-state effects

As follows from Pauling's bonding theory,[54] the exothermicity of the reaction of AA and BB to two molecules AB [equation (5a)] derives from the increased polarity of the resulting bonds. Thus, an 'ionic resonance energy' E_i is introduced in the A—B bond, which is set equal to the square of the difference in electronegativity χ of the atoms A and B [equation (5b); 1 kcal = 4·184 kJ].[54] Consequently, the *BDE* of A—B equals the (arithmetic) mean of the *BDE*s of the homonuclear molecules inclusive the ionic resonance energy of the A—B bond [equation (5c)].

$$\text{A—A} + \text{B—B} \rightarrow 2\text{A—B} \qquad (5a)$$

$$\Delta H_\mathrm{r}\ (\text{kcal mol}^{-1}) = -E_\mathrm{i} = -23(\chi_\mathrm{A} - \chi_\mathrm{B})^2 \qquad (5b)$$

$$BDE(\text{A—B}) = \tfrac{1}{2}BDE(\text{A—A}) + \tfrac{1}{2}BDE(\text{B—B}) + 23(\chi_\mathrm{A} - \chi_\mathrm{B})^2 \qquad (5c)$$

In the case of polyatomic molecules, as shown for the simplest case ABC in equation (6a), the situation modifies slightly. In addition to E_i of the A—B bond, it needs to be considered that E_i of the second bond B—C in the reactants CBB—C and in the products AB—C is also affected. This problem, which has ultimately led to the definition of group electronegativities,[61, 62, 65–68] is related to the fact that the electronegativity of the group AB differs from BBC. Hence, the exothermicity of equation (6a) is a composite of E_i of the A—B bond and the *difference* in E_i of the CBB—C and the AB—C bonds [equation (6b)]. The latter can be viewed as a 'polar relaxation energy' E_relax of the B—C bond, which is caused by the transformation of a non-polar CB—BC bond to the polar A–BC bond. Hence, the *BDE* of the A—BC bond is provided by equation (6c).

$$\text{A—A} + \text{CB—BC} \rightarrow 2\text{A—BC} \qquad (6a)$$

$$\Delta H_\mathrm{r} = -E_\mathrm{i}(\text{A—BC}) - \Delta E_\mathrm{i}(\text{B—C}) = -23(\chi_\mathrm{A} - \chi_\mathrm{BC})^2 - 23[(\chi_\mathrm{AB} - \chi_\mathrm{C})^2 - (\chi_\mathrm{CBB} - \chi_\mathrm{C})^2] \qquad (6b)$$

$$BDE(\text{A—BC}) = \tfrac{1}{2}BDE(\text{A—A}) + \tfrac{1}{2}BDE(\text{CB—BC}) + E_\mathrm{i}(\text{A—BC}) + E_\mathrm{relax}(\text{B—C}) \qquad (6c)$$

For more complex molecules, where the atoms A, B and C may bear additional substituents or groups, the expression becomes more complicated since the changes of the electronegativity differences in all bonds need to be considered, such that the correction term $\sum E_\mathrm{relax}$ needs to be introduced, which provides the sum of the polar relaxation energies, i.e. the sum of all differences in E_i of all bonds *except for the bond which is broken*. This situation refers to the organic molecules in Scheme 1, where the A—BC bond is set equal to the XR—Z bond, and where χ_XR and χ_Z are the *group* electronegativities[61, 62, 65–68] of the organic groups [equation (7)].

$$BDE(\text{XR—Z}) = \tfrac{1}{2}BDE(\text{XR—RX}) + \tfrac{1}{2}BDE(\text{Z—Z}) + 23(\chi_\mathrm{XR} - \chi_\mathrm{Z})^2 + \sum E_\mathrm{relax} \qquad (7)$$

In organic molecules XRZ, the correction term $\sum E_\mathrm{relax}$ refers to the polar relaxation of the XR and Z fragments caused by the formation of the polar R—Z bond. $\sum E_\mathrm{relax}$ covers the contributions of E_i for all bonds in XRZ except for the R—Z bond, i.e. all differences between E_i of the bonds in XRZ and the corresponding bonds in ZZ or XRRX are included. Since the electronegativity difference between the bonding atoms in R and Z will be generally larger than the changes in the group electronegativities imposed upon the more remote bonds in XR and Z (in fact, the latter should be a dilute function of the former), the polar relaxation term should be smaller than the bond polarity contribution, and it will generally serve to increase or decrease E_i of the R—Z bond slightly above or below the value expected from the latter alone. This is in keeping with the general notion that electronegativity effects act importantly only at the atom to which the substituent is attached.[69] For example, use of the group electronegativities from Ref. 66 suggests that the relative energetic contribution of the polar relaxation term is only *ca* 15–30% for the cleavage of the C—H, N—H or C—N bonds in CH_4, NH_3 or CH_3NH_2 (the choice of examples is limited by the reported electronegativities).

According to equation (7), the difference of the *BDE*s of the unsubstituted and the X-substituted systems [equation (8a), Scheme 1] can now be expressed by equation (8b). In the absence of steric ground-state effects of the substituent X [$SSE \approx 0$, equation (3)], which is the case for the presently examined benzylic systems, equation (4) applies. Hence, the covalent and ionic contributions of equation (8b) correspond to the radical stabilization energy (*RSE*) and the polar ground-state stabilization energy (*PSE*) of the substituent X [equations (9) and (10)]. The opposite signs of *RSE* and *PSE* account for the fact that a lower *BDE* results either from a negative *RSE* (radical stabilization) or from a positive *PSE* (polar destabilization), *cf.* Scheme 1 and equations (2) and (4).

$$\Delta BDE = BDE(\mathrm{XR{-}Z}) - BDE(\mathrm{HR{-}Z}) \tag{8a}$$

$$\Delta BDE = \tfrac{1}{2}[BDE(\mathrm{XR{-}RX}) - BDE(\mathrm{HR{-}RH})] + 23[(\chi_{\mathrm{XR}} - \chi_{\mathrm{Z}})^2 - (\chi_{\mathrm{HR}} - \chi_{\mathrm{Z}})^2] + \Delta\Sigma E_{\mathrm{relax}} \tag{8b}$$

$$RSE \equiv \tfrac{1}{2}[BDE(\mathrm{XR{-}RX}) - BDE(\mathrm{HR{-}RH})] \tag{9}$$

$$PSE \equiv 23[(\chi_{\mathrm{HR}} - \chi_{\mathrm{Z}})^2 - (\chi_{\mathrm{XR}} - \chi_{\mathrm{Z}})^2] - \Delta\Sigma E_{\mathrm{relax}} \tag{10}$$

Consequently, the *RSE* of a substituent X [equation (9)] is defined as the relative *BDE* of the symmetrically X-substituted molecule normalized by a factor of $\frac{1}{2}$ to account for the number of radicals formed upon dissociation. This definition is consistent with the experimental work on symmetrical alkanes by Rüchardt and co-workers[3, 8] and with Nicholas and Arnold's conceptual proposal.[47] Moreover, it meets the intuitive requirements that *RSE* should be free of contributions related to the bond polarity and should be independent on the substituent Z. It differs from the original suggestions by O'Neal and Benson[2] and Dewar *et al.*,[70] in that the *BDE* of a symmetrical C—C bond instead of a (polar) C—H bond is taken as reference for the experimental or computational determination of radical stabilization energies. The differences between the choice of the C—H and C—C cleavage reactions for the definition of *RSE* have been addressed by, amongst others, Leroy and co-workers.[4, 5]

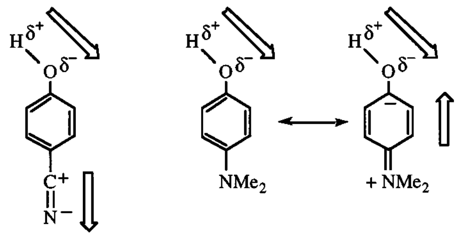
The *PSE*, on the other hand, is described as the difference in ionic resonance energies caused by introduction of the substituent X, i.e. it is a function of the group electronegativities [equation (10)].[61, 62, 65–68] It consists of a 'bond polarity' term related to the change in the electronegativity difference between the atoms in the R—Z bond being broken, and a 'polar relaxation' term, $\Delta\Sigma E_{\mathrm{relax}}$, which describes the relative energetic contributions due to the variations in group electronegativities in the remaining bonds. The significance of the polar relaxation term in equation (10) is that it renders the polar ground-state stabilization a true property of the whole molecule rather than an exclusive property of the broken bond. As noted above, the relative contributions of $\Sigma E_{\mathrm{relax}}$ should be small, such that the difference $\Delta\Sigma E_{\mathrm{relax}}$ is also expected to contribute less than the bond polarity term to the overall *PSE*. For instance, model calculations have been performed by using an established group electronegativity scale.[66] For $\mathrm{XR{-}Z = XCH_2{-}H}$ and $\mathrm{XCH_2{-}F}$ (proximately substituted models for toluenes and benzyl fluorides $\mathrm{XR{-}Z = XC_6H_4CH_2{-}Z}$), the relative contribution of the polar relaxation term to the *PSE* is calculated as 2% and 31% for introduction of X = F.

Qualitative view

According to equation (10), polar ground-state effects exercised by substituents X on the BDEs of benzylic and related bonds can be rationalized in terms of their effects on the group electronegativity of the benzyl group (χ_{XR}), which leads to an increase or decrease in the electronegativity difference of the atoms in the benzylic bond; the concomitant variations in polar effects on the remaining bonds are of secondary importance [$\Delta\Sigma E_{\mathrm{relax}}$ in equation (10)] but can be included to allow a more precise quantitative description. For example, in the case of the benzyl bromides in Scheme 2 the electronegativity of the benzyl fragment is expected to lie below that of bromine, *cf.* Pauling electronegativities of carbon (2.5) and bromine (2.8).[54] Hence, electron-donating aryl substituents lower the electronegativity of the benzyl group further and increase the electronegativity difference of the C—Br bond. A strengthening of the benzylic bond results, which is equivalent to a larger BDE, and the contrary effect is observed for electron acceptors, which enhance the electronegativity of the benzyl group.

Previously, the polar effects on benzylic BDEs have been rationalized in terms of a stabilization or destabilization of the benzylic charge.[30–32, 35] The nature of the interaction between aryl substituents and the benzylic bond was related to hyperconjugation or, preferably, a substituent–dipole interaction. This view (Scheme 2) is probably very similar to the present one, since charge and electronegativity arguments will generally lead to the same predictions, i.e. relative partial atomic charges are also related to the electronegativity difference. However, it should be noted that the effects upon benzylic charges and stabilization of the benzylic bond may also display trends in opposite directions. For example, the introduction of an electron acceptor does not necessarily lead to a more positive atomic charge at a benzylic center, but might well make it more negative on account of the concomitant flow of electron density within the benzylic bonds, which is due to the increased group electronegativity of the benzyl group. In support of this notion, the (charge-dependent) ^{13}C NMR shifts of the α-carbon in benzylic systems show normal or reverse Hammett behavior for toluenes and benzyl halides, respectively.[71–73] Second, while the rationalization by means of electronegativity arguments allows the formulation of relatively simple and intuitive relationships (see below), the quantitative description in terms of variations of atomic charges requires generally the use of calculations[74] or empirical charge–^{13}C NMR shift relationships.[71, 73, 75] Not surprisingly, the consequent analysis in terms of atomic charges becomes complicated even for simple alkanes,[47, 76] and has not been rigorously achieved for benzylic and related systems.[29]

A number of alternative qualitative explanations for polar ground-state substituent effects have been proposed. Bordwell's *et al.* explanation of polar ground-state effects is a slight modification of the charge stabilization argument. Polar ground-state stabilization or destabilization is thought to derive from additive or subtractive combination of dipole moments of the substituent and the broken bond,[37] e.g. for phenols (Scheme 3). While Scheme 3 will mostly lead to the same expectations as the electronegativity arguments, this is



Scheme 3

not always the case, e.g. for *ortho* substituents. The disadvantage of the dipole–dipole interaction argument is that the net dipole moment of the molecule is taken as criterion, while the effect of the substituent on the dipole (electronegativity difference) of the bond to be broken is primarily relevant. In detail, while the vectorial sum of the bond dipoles would be relevant in Scheme 3, equation (10) describes the *PSE* as the sum of all scalar differences in bond dipoles, where the dipole of the broken bond is most important.

According to Zavitsas and Pinto,[44] the higher C–H *BDE* of toluenes, which are substituted with electron acceptors,[46] derives from the fact that the benzylic carbon varies its hybridization in favor or a more electron-donating *p*-type orbital for the C—C bond at the expense of a higher s character, and therefore bond strengthening for the C—H bonds. This thought fails to rationalize the lower *BDE* caused by electron acceptors in other cases, e.g., benzyl bromides (Scheme 2), indicating that rehybridization is not the major energetic denominator of the effects. Another qualitative explanation for the polar effects, which substituents may exert on BDEs, was introduced by Wu and co-workers;[42, 77] it was argued that the stabilization of the toluene or phenol ground states by electron acceptors was due to the fact that the methyl or hydroxy groups in toluene and phenol are donors, such that the introduction of a *para*-acceptor results in a stabilization of the system and, hence, increases the *BDE*. This argument, which is based on the use of a questionable definition reaction for *PSE*,[53] suffers the shortcoming that it focuses on the polar effect which is exercised by the whole aryl group upon the molecule, and not on the polar effect which is related to the particular C—Z bond contained in the aryl group. For example, dealing with compounds such as $XC_6H_4Y^{\delta+}$—$^{\delta-}Z$, the YZ aryl group may act as an electron donor (e.g., for MgCl, HgMe, NHCl, etc.), such that the whole system experiences a net stabilization by the introduction of an electron acceptor X, but the BDE of the $Y^{\delta+}$—$^{\delta-}Z$ bond decreases nevertheless owing to the increased electronegativity of the XC_6H_4Y group, which results in a smaller electronegativity difference in the Y—Z bond; see also Scheme 2.

In conclusion, Pauling's classical bonding theory[54] provides a useful rationale for the polar ground-state stabilization, which affects the *BDE*s according to Schemes 1 and 2. With the available definitions for *RSE* and *PSE* [equations (9) and (10)], further efforts can now be devoted towards an appropriate quantitative interpretation of experimental data.

Quantitative treatment of data—one-bond approximation

Since the polar relaxation energy term ($\Delta\Sigma E_{relax}$) should be small compared with the bond polarity term (see above), it will now be neglected to allow a simpler quantitative description of the polar ground-state effects. Hence, only the energetic contributions of the bond to be broken are considered (*one-bond approximation*) and the simpler equation (11) is obtained.

$$PSE=23[(\chi_{HR}-\chi_{Z})^2-(\chi_{XR}-\chi_{Z})^2]\quad \Delta\Sigma E_{relax}\equiv 0 \qquad (11)$$

Equation (11) can be rewritten by employing more readily apparent molecular characteristics. For example, the intrinsic electronegativity difference between the atoms in the unsubstituted bond HR—Z can be used as reference point, i.e. $\chi_{HR}-\chi_{Z}=\Delta EN$ and deviations therefrom caused by introduction of electron-accepting or -donating substituents X can be expressed in an incremental fashion, i.e. $\chi_{XR}-\chi_{Z}=\Delta EN+\Delta\chi$, where $\Delta\chi$ represents the difference in electronegativity of the groups XR and HR ($\Delta\chi=\chi_{XR}-\chi_{HR}$). Substitution and solution of the binomial term yields the basic expression in equation (12).

$$PSE\ (\mathrm{kcal\ mol^{-1}})=-46[\Delta EN\cdot\Delta\chi+\tfrac{1}{2}\Delta\chi^2] \qquad (12)$$

For many organic systems, the electronegativity difference $\Delta\chi$ caused by exchange of the substituent X in the group R is small compared with the electronegativity difference ΔEN between HR and Z. Assuming that HR bears a carbon center, ΔEN can range up to 1·5, corresponding to the Pauling electronegativity difference between carbon (2·5) and fluorine (4·0),[54, 61] while $\Delta\chi$ is generally much smaller, since the exchange of the substituent in XR causes maximum variations of only *ca* 0·2 units on Pauling's scale,[62, 66] even when X is directly attached like in the carbon-centered groups XR = H—CH_2, F—CH_2, Cl—CH_2, etc. The same should apply for benzylic and related systems, where $\Delta\chi$ represents merely the variations in electronegativity of XR due to the remote aryl substituents, while ΔEN may be much larger for situations involving atoms of different electronegativity, e.g. O—H (phenols), N—H (anilines) and C—Cl (benzyl chlorides). Hence, assuming $\Delta EN \gg \Delta\chi$, the quadratic term ($\frac{1}{2}\Delta\chi^2$) can be neglected, such that one obtains equation (13), which should apply to a variety of experimental situations.

$$PSE\ (\mathrm{kcal\ mol^{-1}})=-46\ \Delta \mathrm{EN}\cdot\Delta\chi\quad \text{for } \Delta EN\gg\Delta\chi \qquad (13)$$

This equation provides important information on the nature of polar ground-state effects. The importance of such effects should increase linearly with the increase in the electronegativity difference of the atoms in the bond being broken (ΔEN) and also with the electronegativity change caused by the introduction of the substituent X ($\Delta\chi$). One can now estimate an upper limit for the magnitude of these effects for organic radicals. When $\Delta EN\approx 1{\cdot}5$ and $\Delta\chi\approx 0{\cdot}2$ are taken as reasonable limiting values (see above), one obtains a range of *ca* 15 kcal mol^{-1} for *PSE*, which compares with typical *RSE*s of up to 20 kcal mol^{-1} per single group attached to a carbon-centered radical.[1, 78] This confirms that polar ground-state effects may readily become significant in relation to radical stabilizing effects.

It is important to recognize that equation (13) is a linear energy relationship, since it describes the linear variation of an energy (*PSE*) as a function of one constant (ΔEN), which is characteristic for the examined unsubstituted system HR—Z and independent of the substituents X, and another parameter ($\Delta\chi$), which varies with the substituent X, but is independent of the system. For the examination of benzylic and related systems, where the polarity of the broken bond is sufficiently high to allow the approximation $\Delta EN\gg\Delta\chi$, one can now substitute ΔEN and $\Delta\chi$ by the reaction constant ρ and an aryl substituent parameter σ [equations (14a) and (14b)] to afford the Hammett-type relationship in equation (15). The use of equation (15), a linear *free* energy relationship, instead of equation (13), a linear energy relationship, is subject to the justifiable assumption (see Computational Details) that substituent-dependent entropy contributions to the *PSE* are negligible.[79] With respect to equation (14b) it should be noted that correlations between substituent constants and electronegativity are known:[80]

$$\rho\propto-\Delta EN \tag{14a}$$

$$\sigma\propto\Delta\chi \tag{14b}$$

$$PSE(\mathrm{X})=\rho\sigma \qquad \text{for } \Delta EN\gg\Delta\chi \tag{15}$$

A second limiting situation is the action of substituents X on a non-polar bond HR—Z, where $\Delta EN\approx 0$. The resulting equation [$PSE(\mathrm{X})=-23\Delta\chi^2$] can be transformed by use of equation (14b) to provide the quadratic dependence of the *PSE* on the σ substituent parameter in equation (16) (a=constant); thus, both electron acceptors and donors increase the *PSE* since both introduce polar character into the XR—Z bond. Since the *PSE* for a system with non-polar bond is only determined by the quadratic term ($-23\Delta\chi^2$), which has been deemed negligible for bonds with high polarity (see above), one may conclude that polar ground-state effects caused by the same set of substituents X are much smaller for a non-polar bond with $\Delta EN\approx 0$ compared with their effects on a very polar bond where $\Delta EN\gg\Delta\chi$. Thus, if the variation in group electronegativities of carbon-centered groups XR is again estimated as *ca* 0.2 (see above), the polar ground-state effects in non-polar bonds would be restricted to *ca* 1 kcal mol^{-1} according to equation (13), which compares with a maximum effect of *ca* 15 kcal mol^{-1} for very polar bonds (see above).

$$PSE(\mathrm{X})=-a\sigma^2 \qquad \text{for } \Delta EN\approx 0 \tag{16}$$

Finally, for the intermediate situation where $\Delta EN\approx\Delta\chi$, equation (12) needs to be explicitly evaluated or can be transformed by means of equation (14b) to yield the second-order polynomial dependence on the substituent parameters σ shown in equation (17) (b, c=constant).

$$PSE(\mathrm{X})=b\sigma-c\sigma^2 \tag{17}$$

Comparison with experimental data

As was demonstrated above, Pauling's bonding and electronegativity theory justifies the application of simple Hammett-type relationships for the quantitative treatment of the *PSE*s in benzylic and related bonds. Depending on the polarity of the broken bond (ΔEN), plots of the PSE for different aryl substituents *versus* the substituent parameters σ should be linear, parabolic or curved. The three situations expected from equations (15)–(17) are schematically displayed in Figure 1. Experimentally, only situations for linear behavior have been observed. Hence, for the aryl-substituted phenylacetonitriles **1**,[18, 19] phenols **2**,[11, 37, 39] anilines **3**,[20] fluorenes **4**,[18, 21] phenylazoalkanes **6**,[26–28, 41] dibenzylmercury compounds **7**,[30–32] anisoles **9**,[34] benzyl bromides **10**[35] and thiophenols **11**,[37] satisfactory correlations between *BDE*s and σ constants have been observed. Hammett's σ parameters, Brown's σ^+ values or Taft's inductive σ constants were chosen for correlation. The *BDE*s for the different aryl substituents could be employed either directly in the Hammett plots, which would suggest that polar ground-state effects are dominant, or after correction for radical contributions. The observed linear correlations suggest that the requirement of equation (15) ($\Delta EN\gg\Delta\chi$) is met for the experimentally examined systems.

The second requirement imposed by equation (15) for the cleavage of polar bonds is that the ρ values obtained from

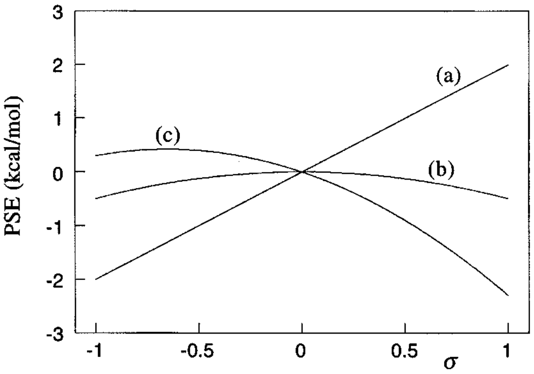


Figure 1. *A priori* expectations for the possible dependence of the polar ground-state stabilization energy (*PSE*) as a function of the substituent parameter σ. (a) Calculated using equation (15) with ρ=2 for a situation where $\Delta EN\gg\Delta\chi$. (b) Calculated using equation (16) with a=0·5 for a situation where $\Delta EN\approx 0$. (c) Calculated using equation (17) with $b=-1{\cdot}3$ and c=1 for a situation where $\Delta EN\approx\Delta\chi$

the linear Hammett plots should increase linearly with the electronegativity difference (ΔEN) of the atoms forming the benzylic bond [equation (14a)]. Interestingly, a linear relationship between the σ constants obtained from the various BDE–σ plots and ΔEN (using the covalent potential modified by Benson or Pauling's scale as a measure of electronegativity)[58] has been scrutinized previously.[35, 37, 48] However, the lack of an *a priori* reason for this linear correlation has been emphasized,[35] which rendered the proposed relationship empirical. The proportionality between ρ values and ΔEN required by equation (14a) provides a possible rationale for this experimentally observed relationship. Nevertheless, the experimental plot should be considered with some caution, since its intercept is substantial. The latter would suggest substantial polar ground state effects ($\rho = 3{\cdot}44$)[37] even for non-polar bonds, which is clearly not expected from the above arguments [equation (14a)]. Moreover, the contributions of the *RSE*s to the *BDE*s are uncertain for some systems, such that an appropriate correction of the *BDE*s for radical stabilizing effects is difficult.

For the cleavage of virtually non-polar bonds, Hammett plots of the *PSE* should show a parabolic appearance [equation (16), Figure 1]. Experimentally, this would be an interesting scenario, since the BDE could increase, according to equation (4), for both electron donors and acceptors. In contrast, since most electron acceptors but also donors are thought to stabilize radicals, one would expect a decrease in the BDEs for both types of substituents. However, an experimental situation, where both electron donors and acceptors increase the BDE of a benzylic bond on account of the introduction of polar character into a non-polar bond [equation (16)] has not been reported, to our knowledge. Supposedly, the lack of experimental evidence is due to the fact that the substituent effects on the *RSE* are larger than the polar ground-state effects, since the latter are expected to be small ($<1\ \mathrm{kcal\ mol^{-1}}$, see above) for the cleavage of nonpolar bonds ($\Delta EN \approx 0$), e.g. in the homolysis of the relatively non-polar C—C bond of the cyclopropanes **5**.[22–25]

Finally, situations involving bonds of intermediate polarity [equation (17)] should result in a curvature of the PSE plots (Figure 1). While experimental data in favor of a pronounced curvature in Hammett plots for radical reactions appear again to be elusive, this might in part be due to the judicious choice of the substituent parameters (σ, σ^+, σ_0, etc.), and a restricted range of examined substituents. It should be noted, however, that second-order polynomial dependences on σ parameters have been employed previously.[81]

Comparison with computed data

The use of equations (8a) and (10) allows the transformation of equation (8b) to equation (18), which provides in principle a method for the *experimental* determination of PSEs through the measurement of four *BDE*s of the polar XR—Z and non-polar XR—RX bonds, each with references to the unsubstituted systems HR—Z and HR—RH. As was outlined previously,[53] the BDEs in equation (18) can be expressed as enthalpic differences [equation (19)] to allow also a computational assessment of PSEs. Thus,

$$\begin{aligned} PSE = {} & \tfrac{1}{2}[BDE(\mathrm{XR{-}RX}) - BDE(\mathrm{HR{-}RH})] \\ & - [BDE(\mathrm{XR{-}Z}) - BDE(\mathrm{HR{-}Z})] \qquad (18) \end{aligned}$$

$$\begin{aligned} PSE = {} & [\Delta H_\mathrm{f}(\mathrm{XR{-}Z}) - \Delta H_\mathrm{f}(\mathrm{HR{-}Z})] \\ & - \tfrac{1}{2}[\Delta H_\mathrm{f}(\mathrm{XR{-}RX}) - \Delta H_\mathrm{f}(\mathrm{HR{-}RH})] \qquad (19) \end{aligned}$$

PSEs are obtained from calculated ground-state energy differences ($\Delta\Delta H_\mathrm{f}$) for the symmetrically substituted alkanes and the examined Z-substituted systems (Figure 2). Note that both components of the *PSE*, namely the bond polarity term and the polar relaxation term [equation (10)], are implicitly included in the computed data. Equation (19) represents the thermodynamic equivalent of an isodesmic reaction,[82] shown for the general and the benzylic case in equations (20a) and (b).

$$\mathrm{XR{-}RX + 2HR{-}Z \rightarrow HR{-}RH + 2XR{-}Z} \qquad (20a)$$

$$\begin{aligned} & \mathrm{XC_6H_4CH_2{-}CH_2C_6H_5X + 2C_6H_5CH_2{-}Z \rightarrow} \\ & \qquad \mathrm{C_6H_5CH_2{-}CH_2C_6H_5 + 2XC_6H_4CH_2{-}Z} \qquad (20b) \end{aligned}$$

The isodesmic reaction (20b) was employed to confirm the theoretically predicted trends of the *PSE*s (Figure 1), and in particular to search for systems which would show parabolic or curved Hammett plots. The AM1 method[83] was selected as a representative procedure,[53] since it yields *BDE*s close to the experimental values.[50] To substantiate the relationships required by equations (15)–(17), the sub-

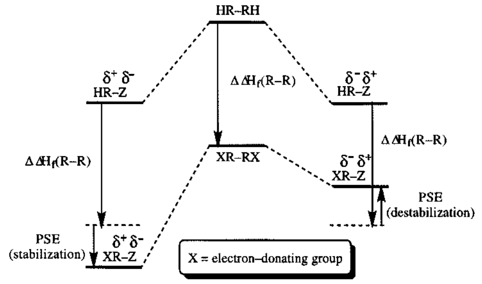


Figure 2. Enthalpic effect for the introduction of polar bond character, which results in a relative stabilization, independent of whether the electronegativity of the attached group Z exceeds (left) or lies below (right) that of the group R. When an electron donor X is attached to the group R, the electronegativity of the latter decreases. Thus, the electronegativity difference increases in one case (left) but decreases in the other (right), relative to the unsubstituted system. This results in a *relative* polar stabilization or destabilization of the system due to X. The related polar ground-state stabilization energies (*PSE*s) are obtained by comparing the differences in heats of formation with the non-polar case (middle). Note that the correction factor $\frac{1}{2}$ [equation (19)] is omitted for the sake of clarity

stituent dependence of the *PSE* was calculated for benzyl alcohol, toluene and phenylborane[53] as examples for systems where a highly polar C—O, a slightly polar C—H or a virtually non-polar B—H bond is broken (*cf.* Pauling electronegativities for C = 2·5, O = 3·5, H = 2·1 and B = 2·0).[54, 61] The calculated *PSE*s were plotted against various σ values (σ, σ^+, σ^-) and other inductive and resonance substituent parameters.[84] The use of Hammett's σ values provided the correlations with the least scatter when fitted according to equations (15)–(17) and the best overall agreement with theoretical expectations. The calculated data were then fitted by a linear, quadratic or second-order polynomial function (Figure 3)).

The comparison with the theoretically expected behavior (Figure 1) demonstrates that all basic situations, i.e. linear, parabolic and curved, can be reproduced by calculations (Figure 3). Furthermore, polar ground-state effects are very small (0.1 *versus* 1 $\mathrm{kcal\,mol^{-1}}$) for the parabolic case involving cleavage of a virtually non-polar bond. This reduced sensitivity towards polar effects is indeed expected from the arguments presented above. The calculated parabolic or curved functions encourage the search for experimental manifestations. In particular, since the computed *PSE*s for toluenes predict a significant curvature in the Hammett plot, it would be interesting to verify this behavior experimentally. Unfortunately, the available *BDE*s for toluenes (X = *p*-Me, *t*-Bu, *m*-Me, *p-Cl*, *m*-Cl, *m*-Br) are too limited to draw an unambiguous conclusion, since values for strong electron donors, which would make the curvature most readily apparent, are not available[45, 46] (note that the region of electron acceptors in Figure 3 could also be satisfactorily fitted by a linear function).

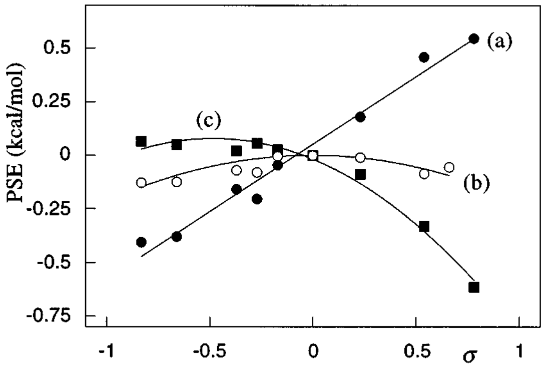


Figure 3. Calculated (AM1 method) dependence of the polar ground-state stabilization energy (*PSE*) as a function of the substituent parameter σ for (a) benzyl alcohol, (b) phenylborane and (c) toluene. The PSEs were obtained from the isodesmic reaction 20b using the AM1 method and representative *para*-substituents (*p*-NMe_2, *p*-NH_2, *p*-OH, *p*-OMe, *p*-Me, *p*-Cl, *p*-CF_3, *p*-CN and *p*-NO_2). The fits for benzyl alcohol, phenylborane and toluene are based on linear, quadratic and second-order polynomial functions, respectively; *cf.* theoretically expected situations in Figure 1 and equations (15)–(17)

While the qualitative trends observed by the AM1-calculated PSE data are reassuring (*cf.* Figures 1 and 3), it must be kept in mind that the quantitative agreement between the experimental[35, 37] and AM1-calculated[53] ρ values, e.g. $-3{\cdot}2$ *versus* $-1{\cdot}69$ for thiophenol and $+5{\cdot}5$ *versus* $+0{\cdot}68$ for benzyl bromide, is poor, which warrants the examination by more sophisticated computational methods. Another reason for the discrepancy could lie in the circumstance that the calculated data refer to the gas phase, but the experimental data to the liquid phase. Little is known about the sensitivity of *PSE* towards solvation or solvent polarity, but experimental data for phenols do actually reveal unexpectedly large variations on going from the vapor to the liquid phase as well as changes with solvent polarity, which might be in part due to differences in *PSE*.[49, 85]

Relationship to the kinetics of radical reactions

The values for the bond dissociation energy (*BDE*), polar ground state stabilization energy (*PSE*) and radical stabilization energy (*RSE*) (*cf.* Scheme 1) provide enthalpic information on radical reactions. A major amount of data has been accumulated on the kinetics of radical reactions (rate constants, activation energies) and in order to apply the present enthalpic model to predict trends in radical kinetics two limitations need to be taken into account.

First, the transition states in radical reactions may experience an additional charge-transfer stabilization, which itself is commonly called the 'polar effect' in radical reactions.[86–92] In fact, to differentiate from this charge-transfer stabilization of transition states, the presently evaluated enthalpic effects of substituents on the bond dissociation energy are more accurately referred to as polar *ground-state* effects and the related stabilization energy is termed polar *ground-state* stabilization energy (*PSE*). Second, as expected from the Evans–Polanyi relationship,[63, 64] the transition state of radical reactions experiences only part of the enthalpic effects; further, the degree varies depending on the reaction class and on whether the transition state is early or late.[3, 6, 7] When the transition state for radical cleavage is relatively late and not stabilized by charge-transfer interactions (this is expected in most endothermic bond homolyses), there is good experimental evidence that the measured rate constants are strongly influenced by polar ground-state effects. In these limiting situations, the proposed electronegativity model and the method of calculation may successfully predict the direction (negative or positive ρ value) of the polar effect on the kinetics of the radical reaction. Accordingly, the polar effects in the thermolysis of azoalkanes **6** and dibenzylmercury compounds **7** have been attributed to and taken as evidence for polar *ground-state* effects in the C—N or C—Hg bond cleavage.[30–33, 36, 41]

When charge-transfer stabilization of the transition state becomes important, the enthalpic model and its predictions for radical kinetics must be applied with caution, since the additional stabilization of the transition state may work in the same or in the opposite direction as the polar ground-state effect, such that the polar effect observed in kinetic measurements may be different from the polar effect on the energetics (BDE). In these cases, it is not straightforward to decide on whether polar ground-state or polar transition state effects dominate.[92] For example, in the case of toluenes, this happenstance has led to a vivid and still not entirely resolved debate,[10, 44–46, 87, 93–95] on whether the kinetically observed polar effect originates from the ground state or from the transition state stabilization. However, whenever the expected polar stabilization of the transition state is opposite to the experimentally observed one,[41] or when the direction of the polar effect on the kinetics changes with the choice of the reaction partner, e.g. a hydrogen-abstracting agent,[10, 87, 93, 94] good arguments for the predominant involvement of either effect can be brought forward, and these have been employed to assign the polar effects in the thermolysis of azoalkanes **6** to ground-state effects,[41] but the polar effects with positive ρ values in the hydrogen abstraction from the toluenes **8** to chanrge-transfer transition-state effects.[10, 87, 93, 94]

CONCLUSIONS

The relative contributions of polar and radical substituent effects in organic radical reactions, in particular for aryl-substituted systems, have been under intensive investigation and it has been questioned whether a meaningful separation is at all possible,[1, 35, 43] since steric, polar and radical substituent effects may all be operative to varying degrees in the ground and transition states. The present treatment, which is based on simple electronegativity arguments, allows the differentiation and quantification of polar ground-state and radical effects by means of computed data or through correlation analysis of experimental data. It is based on the definition of *RSE* as the *BDE* of the non-polar bonds in symmetrically substituted molecules, and polar ground-state effects are understood as deviations related to the substituent-dependent increase or decrease in bond polarity.

The results allow one to express *a priori* predictions on the importance of polar ground state effects and to rationalize better previous experimental results. In particular, the interpretation according to Pauling's bonding theory accounts for the observed linear Hammett relationships, which have been reported for the *BDE*s or radical kinetics of many benzyl-type systems,[11, 18–21, 26–45] and for the linear correlation between Hammett ρ values and the electronegativity difference between the atoms forming the benzylic bond.[35, 37] The original Hammett σ substituent constants appear to be useful in correlating polar ground-state effects, since they provide for linear free energy correlations of the calculated and experimental data in many cases. In other cases, deviations from linearity are noted, which are expected for situations involving the cleavage of less polar or non-polar bonds. The calculated and experimental data can be accounted for by the use of the one-bond approximation in equations (15)–(17), which neglects contributions due to the polar relaxation energy; at present, it is not known to what extent the latter contributes.

COMPUTATIONAL DETAILS

The AM1 method[83] included in the MacGAMESS (MOPAC) program package[96] run on a PowerMacintosh personal computer was employed. The *PSE*s were calculated from equation (19), which required the calculated heats of formulation for four molecules: the X-substituted molecule (XR—Z), the unsubstituted molecule (HR—Z), the X-substituted dimer (XR—RX), and the unsubstituted dimer (HR—RH). The molecular geometries were fully optimized. *p*-NMe_2, *p*-NH_2, *p*-OH, *p*-OMe, *p*-Me, *p*-Cl, *p*-CF_3 and *p*-NO_2 [*p*-CN] were selected as representative aryl substituents. The data contained in Figure 3 are not corrected for zero-point vibrational or thermal energy contributions. The inclusion of the latter is not expected to be significant for an isodesmic reaction like equation (20).[82] Indeed, as was representatively checked for benzyl alcohol and toluene, zero-point vibrational or thermal energy corrections (using AM1-calculated vibrational frequencies and standard thermodynamic enthalpies at 298 K) did not cause a change in the qualitative appearance of the Hammett plots, nor were the variations of the absolute PSEs noteworthy ($<0{\cdot}05$ kcal-mol^{-1}). It was also demonstrated that the use of the free energy instead of the enthalpy of the isodesmic reaction (19) as a measure of the *PSE* (including the AM1-calculated internal entropies at 298 K) caused no significant changes ($<0{\cdot}05$ kcal mol^{-1}). The latter finding justifies the application of Hammett-type relationships, i.e. the transformation of equation (13) to equation (15) (see text).

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