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Variable Trends in R–X Bond Dissociation Energies (R = Me, Et, *i*-Pr, *t*-Bu)

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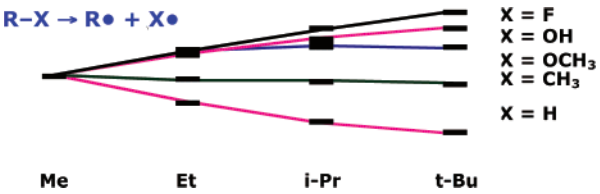
ABSTRACT



High level ab initio molecular orbital calculations confirm experimental indications that the effect of alkyl substituents (R = Me, Et, *i*-Pr, *t*-Bu) on R–X bond dissociation energies varies considerably according to the nature of X. A simple qualitative explanation in terms of valence-bond theory is presented, highlighting the increasing importance of the stabilization of R–X by the ionic R^+X^- configuration for electronegative X substituents (such as F, OH, and OCH_3).

It has long been held that the relative "stabilities" of alkyl radicals increase in the order Me < Et < *i*-Pr < *t*-Bu, with the increasing stability being primarily attributed to the stabilizing effect of additional methyl groups interacting by hyperconjugation with the radical center.[1] However, radical stability is a loosely defined concept because strictly speaking the stabilities of nonisomeric entities of any kind are not directly comparable. When the stabilities of nonisomeric alkyl radicals are compared, this has to be done using some reference reaction whose choice necessarily introduces an element of arbitrariness. Thus the traditional ordering of the stabilities of the alkyl radicals is often derived from their relative R−H bond dissociation energies (BDEs). However, as has long been noted,[2,3] if radical stabilities were instead to be defined using an alternative reference reaction (such as the R−OH BDEs), different conclusions concerning their relative stabilities would be reached. In fact, in very interesting recent articles, Zavitsas[4,5] points out that for some reference reactions, the *reverse* ordering of alkyl radical stabilities results. Nonetheless, the concept that (because of hyperconjugative effects) the intrinsic stability of the alkyl radicals increases from Me to *t*-Bu has proven to be extremely useful in explaining the kinetics and thermodynamics of many chemical reactions.

The R−X BDEs are of fundamental importance, and we feel that further examination is warranted. There are two primary purposes for the present article. First, we use high-level ab initio calculations,[6] specifically at the G3(MP2)-RAD level,[7] to obtain reliable R−X BDEs. Experimental thermochemical data involving radicals are notoriously difficult to obtain accurately, and there is the danger that trends in sequences such as Me, Et, *i*-Pr, and *t*-Bu might be masked by uncertainties arising from data emanating from

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[1] See, for example: March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*; McGraw-Hill: New York, 1963; p 153.

[2] Benson, S. W.; Shaw, R. *Adv. Chem. Ser.* **1968**, *75*, 287−294.

[3] Rüchardt, C. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 830−843.

[4] Zavitsas, A. A. *J. Chem. Educ.* **2001**, *78*, 417−419.

[5] Matsunaga, N.; Rogers, D. W.; Zavitsas, A. A. *J. Org. Chem.* **2003**, *68*, 3158−3172.

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a variety of experimental sources. The high-level theoretical calculations, on the other hand, are likely to produce reasonable absolute results, but more significantly, they should produce even more accurate *trends* because the uniform treatment enhances the prospect of a cancellation of errors. Second, we rationalize the results with the aid of simple valence-bond arguments. To this end, we calculate R−X BDEs as well as the ionization energies (IEs) and electron affinities (EAs) of R and X for a range of R−X systems, with R = Me, Et, *i*-Pr, and *t*-Bu, and X = H, CH_3, OCH_3, OH, and F.[8]

The R−X BDEs for R = Me, Et, *i*-Pr, and *t*-Bu and X = H, CH_3, OCH_3, OH, and F are shown in Table 1, and the relative values (highlighting the alkyl substituent effect) are plotted in Figure 1. From these results it is clear that the strong *decrease* (with increasing alkylation) in the BDE for X = H is in fact an extreme case. For X = CH_3, there is also a monotonic decrease but the overall change (from Me to *t*-Bu) is less than 5 kJ mol^{-1}. More striking are the results for the alcohols and fluorides, for which the BDEs *increase* strongly with increasing alkylation. The ethers present an interesting intermediate situation, showing an increase from Me to *i*-Pr but then a plateauing (actually a small decrease) from *i*-Pr to *t*-Bu. Our results clearly confirm the earlier observations[2−5] that, if BDEs are used to measure radical stabilities, then vastly different conclusions are reached for the relative stabilities of the alkyl radicals, depending upon the reference reaction.

Table 1. Effect of Alkyl Substituents (R = Me, Et, *i*-Pr, *t*-Bu) on R−X Bond Dissociation Energies (0 K, kJ mol^{-1})[a]

	R−H	R−CH_3	R−OCH_3	R−OH	R−F
Me	428.4	361.0	340.3	370.6	452.5
Et	414.3	359.4	352.6	381.7	465.8
i-Pr	404.4	358.4	356.1	389.9	476.9
t-Bu	398.7	356.6	355.2	395.6	485.7

[a] Calculated at the G3(MP2)-RAD level of theory and including scaled B3-LYP/6-31G(d) zero-point vibrational energy corrections.

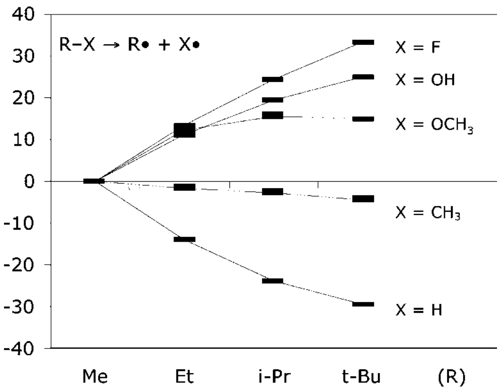

Figure 1. The relative R−X BDEs (kJ mol^{-1}) for R = Me, Et, *i*-Pr, and *t*-Bu and X = H, CH_3, OCH_3, OH, and F.

The unusual nonmonotonic ordering of the radical stabilities for the ethers, which we have also observed for both the barriers and enthalpies in the β-scission of $ROZ^{\bullet}$ radicals (where Z = CH_2, $C(SCH_3)_2$, and $C(SCH_3)SCH_2OCOCH_3$),[9] suggests that the R−X BDEs are the result of two competing effects. The first is the increasing “stability” of the alkyl radicals from Me to *t*-Bu, which serves to lower the BDEs in that order. The second is the increasing “stability” of the R−X compounds, which also appears to increase in the order Me to *t*-Bu and which leads to a corresponding increase in the BDEs. Thus, in the R−H and R−CH_3 compounds the $R^{\bullet}$ stability effect appears to be dominant (though to different extents), whereas in the R−OH and R−F compounds the R−X stability effect now appears dominant, with the ethers representing an intermediate case.

To explore the origin of the stabilizing effect of increasing alkylation in the R−X compounds, we examined the R−X bond lengths (Table 2), the natural bond orbital (NBO) charges on X in the R−X compounds (Table 3), and the vertical ionization energies and electron affinities of the $R^{\bullet}$ and $X^{\bullet}$ fragments (Table 4).

Table 2. Effect of Alkyl Substituents (R = Me, Et, *i*-Pr, *t*-Bu) on R−X Bond Lengths (Å)[a]

	X = H	X = CH_3	X = OCH_3	X = OH	X = F
Me	1.093	1.531	1.410	1.419	1.383
Et	1.096	1.532	1.417	1.425	1.393
i-Pr	1.099	1.535	1.428	1.431	1.404
t-Bu	1.101	1.540	1.442	1.439	1.416

[a] Based on B3-LYP/6−31(d) optimized geometries.

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(6) Standard ab initio molecular orbital calculations were performed using the GAUSSIAN 98 and MOLPRO 2000.6 software packages: (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98*; Gaussian, Inc.: Pittsburgh, PA, 1998. (b) Werner, H.-J.; Knowles, P. J.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.; Schütz, M.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. *MOLPRO* 2000.6; University of Birmingham: Birmingham, 1999.

(7) An assessment of the reliability of this level of theory can be found in: Henry, D. J.; Parkinson, C. J.; Radom, L. *J. Phys. Chem. A* **2002**, *106*, 7927−7936.

(8) Unless otherwise noted, IEs and EAs were calculated at a modified G3(MP2)-RAD level of theory, G3(MP2)-RAD(+), in which the URCCSD-(T) and corresponding RMP2 calculations are performed with the 6-31+G-(d) basis set instead of the normal 6-31G(d) basis set.

(9) Coote, M. L.; Radom, L. *Macromolecules.* Submitted for publication.

Table 3. Effect of Alkyl Substituents (R = Me, Et, *i*-Pr, *t*-Bu) on NBO Charges on X in R−X Species[a]

	X = H[b]	X = CH_3	X = OCH_3	X = OH	X = F
Me		0.000	−0.298	−0.282	−0.387
Et		0.008	−0.303	−0.285	−0.393
i-Pr		0.018	−0.309	−0.289	−0.400
t-Bu		0.028	−0.317	−0.294	−0.407

[a] NBO charges calculated at the RMP2/G3(MP2)Large level. [b] The NBO charges for the hydrogen atoms in the X = H systems are not included because they differ significantly from AIM charges, which reveal a negligible polarization of the C−H bond in all these cases.

Table 4. Vertical Ionization Energies (IEs) and Electron Affinities (EAs) for R• and X• (0 K, eV)[a]

R	IE	EA	X	IE	EA
Me	9.76	−0.06	H	13.66	0.74[b]
Et	8.63	−0.47	OCH_3	10.90	1.35
i-Pr	7.83	−0.63	OH	13.00	1.68
t-Bu	7.26	−0.48	F	17.42	3.30

[a] Calculated at the G3(MP2)-RAD(+) level of theory, unless otherwise noted. [b] Calculated at the G3(MP2)-RAD(++) level of theory so as to include diffuse functions on H in the underlying 6-31++G(d,p) basis.

Examining first the R−X bond lengths (Table 2), we observe that within each series the R−X bond length increases in the order Me < Et < *i*-Pr < *t*-Bu. Interestingly, this trend occurs regardless of whether the R−X bond strength itself increases or decreases in that order. For X = H and Me the bond length changes reflect the normal pattern for covalent bonding where the longer bond is generally also the weaker bond and derives from the more delocalized character of the bonding electron in R. Increasing steric strain in R−X as R is made more bulky, at least for the bulkier X groups (X = CH_3 and OCH_3), would further reinforce this tendency of longer bonds for larger R (and could also contribute to variations in BDEs). For X = F and OH, however, a more unusual trend is observed. Specifically, changing R from Me to *t*-Bu leads to both longer *and* stronger bonds. This appears to reflect the growing ionicity of the R−X bond (discussed below). Ionic bonds, where orbital overlap is not required, tend to be longer than covalent bonds where overlap is a prerequisite to bonding.

Let us now address the energetic consequences associated with variation in the R group. One possible origin for the stabilizing effect of larger R in R−X with X = OCH_3, OH, and F could be hyperconjugative donation from the lone pair electrons on X to the alkyl group pseudo-π^* orbitals, which would be predicted to increase in importance from Me to *t*-Bu. However, if hyperconjugative factors were dominant, one would expect the R−X bond length to *decrease* with increasing alkylation, as a result of increasing double-bond character. The observation that the R−X bond length increases with increasing alkylation (Table 2) suggests that, although they may well contribute to the overall trends in the R−X BDEs, hyperconjugative factors are not likely to provide the *main* explanation for the stabilizing effect of R in R−X compounds.

Examining next the charges (Table 3), two key observations may be made. First, the electronegative X substituents (i.e., OCH_3, OH, and F) lead to a substantial polarization of the R−X bond, with the alkyl group donating electrons to the electronegative X fragment. In contrast, in the R−H and R−CH_3 cases, the charge separation across the R−X bond is relatively small. Furthermore, the increasing negative charge on X in R−X qualitatively reflects the increasing electron affinity of $X^•$, with H and CH_3 having relatively low values, OCH_3 and OH having moderate values, and F having a relatively high value (see Table 4). Second, for electronegative X, the amount of polarization increases monotonically within an R−X series from Me to *t*-Bu (see Table 3). This increasing charge on R in R−X reflects the increasing electron-donating capacity of $R^•$, as measured, for example, by its decreasing ionization energy (see Table 4).

The changes in ionic character for the R−X bond as R and X are varied can provide a simple qualitative explanation for the relative R−X BDEs. In valence-bond theory, the R−X bond can be thought of as a resonance hybrid of the following contributing resonance structures:

$$R{:}X \leftrightarrow R^+X^- \leftrightarrow R^-X^+ \qquad (1)$$

The extent to which the alternative configurations contribute is determined by their relative energies. Thus, in a hypothetical pure covalent bond, the ionic structures are high in energy and do not contribute, whereas in a hypothetical pure ionic bond, one of the alternative ionic forms is substantially lower in energy than the other contributing structures.[10] When multiple configurations are relatively close in energy, the mixing of these configurations leads to a substantial lowering of the bond energy. This stabilizing effect is predicted to become more significant as the relative energy of the ionic form decreases, and the mixing between the ionic and covalent forms increases.[11]

Applying these ideas to the R−X BDEs of the present work leads us to reaffirm Zavitsas' conclusions regarding the importance of R−X bond polarity in determining R−X bond strength, reached on the basis of Pauling's electronegativity equation.[5] We recall that there is a substantial polarization of the R−X bond (in the R^+X^- direction) for the more electronegative substituents (OCH_3, OH, and F) but not for the less electronegative substituents (H and CH_3). We therefore expect that the ionic R^+X^- configuration should contribute to a substantial stabilization of the R−X bonds in the former but not the latter cases. In addition, we recall that, within each series, the polarization increases as R is

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(10) Pross, A. *Theoretical and Physical Principles of Organic Reactivity*; John Wiley & Sons: New York, 1995.

(11) Situations in which the bond energy is dominated by resonance between the covalent and ionic contributions have been named "charge-shift bonding" by Shaik, Hiberty, and co-workers. For more detailed discussions of this effect, see for example: (a) Shaik, S.; Maitre, P.; Sini, G.; Hiberty, P. C. *J. Am. Chem. Soc.* **1992**, *114*, 7861−7866. (b) Galbraith, J. M.; Blank, E.; Shaik, S.; Hiberty, P. C. *Chem. Eur. J.* **2000**, *6*, 2425−2434. (c) Shurki, A.; Hiberty, P. C.; Shaik, S. *J. Am. Chem. Soc.* **1999**, *121*, 822−834.

varied from Me to *t*-Bu. Hence, when it is significant, we expect the stabilizing influence of the ionic configurations to increase in the order Me < Et < *i*-Pr < *t*-Bu. This stabilizing effect, can therefore account for the *increase* (rather than expected decrease) in the R−X BDEs with increasing alkylation in the R−OCH_3, R−OH, and R−F molecules. Note that the lack of polar character in R−X when X = CH_3 does not necessarily imply negligible ionic character in the R−CH_3 bond. In that case almost equal contributions of R^+X^- and R^-X^+ forms would mean that any charge effects would largely cancel out so that ionic mixing, though present, would only have energetic consequences. Such contributions would stabilize the R−X bond for the X = CH_3 series, and this provides an explanation for the substantial difference in the BDE trends for X = CH_3 vs X = H.

In conclusion, high-level ab initio molecular orbital calculations confirm that the effect of alkyl substituents (R = Me, Et, *i*-Pr, *t*-Bu) on R−X bond dissociation energies varies considerably according to the nature of X. In particular, the usual ordering of the R−H BDEs (Me < Et < *i*-Pr < *t*-Bu) is reversed when X is an electronegative substituent such as F or OH. This effect of X can be understood in terms of the increasing contribution of the ionic R^+X^- configuration for electronegative X substituents. Such stabilization of R−X increases with increasing alkylation and leads to an increase in the R−X BDEs, despite the accompanying increase in what is loosely (but usefully) termed $R^\bullet$ radical stability.

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