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Carbon−Carbon Bond Cleavage in Radical Anions of Strained Diphenylethane Derivatives

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Abstract: Fragmentation reactions of radical anions (mesolytic cleavages) of 1,1,2,2-tetraalkyl-1-(4′-nitrophenyl)-2-phenylethanes with varying degrees of steric strain have been studied in polar solvents. The rates and activation parameters obtained were compared to the corresponding values obtained for homolytic bond scissions in the neutrals. The free energies of activations for both types of reactions strongly depend on the strain present in the molecule. With the exception of the most crowded members of the series, nearly all of the strain is released in the transition state of homolytic reactions, and ca. 77% of it is relieved in the transition states of mesolysis. The mesolytic fragmentations have activation energies that are on average ca. 12.5 kcal/mol lower than the homolytic processes. The observed redox activation is shown to have thermodynamic origins.

Unimolecular fragmentations of radical ions to yield radicals and ions (mesolytic cleavages) constitute elementary steps of many electron-transfer-initiated processes.[1−3] In the case of reductive cleavages, where the radical anions are the reactive intermediates, polar carbon−heteroatom bonds undergo scissions most readily.[2,3] The rates of these reactions are usually significantly faster than those observed for the homolytic cleavage of the same bonds in neutral substrates.[4,5] Such "bond activations" have thermodynamic origins, and provide a general low-activation-energy alternative mode of braking single bonds.[1,4,5] Despite the fact that C−C bonds are central to organic chemistry, and that many reductive bond-breaking[6−8] (e.g., dissolving metal reductions) or bond-making (e.g., $S_{RN}1$ reac-

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tions[7]) procedures are known, the quantitative mechanistic understanding of C−C mesolytic cleavages is still incomplete.[5,8,9]

We have undertaken a detailed study of C−C bond fragmentation in radical cations[10] and anions[9] using sterically crowded diphenylethane derivatives in order to delineate the critical mechanistic features of such reactions. Our studies involve probing of strain and solvent effects as well as exploration of the relationship between thermodynamics and kinetics of these processes.[5a,11] A quantitative comparison of mesolysis with the better known homolysis or heterolysis[5b] should provide an insight into the elementary process of bond making/breaking.

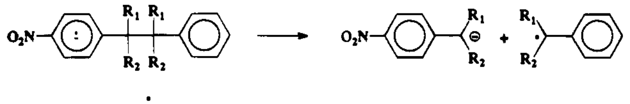
By design, the unpaired electron in our radical anions is initially strongly localized in the π-system of the nitrophenyl moiety. The bond fragmentation requires that the excess of the electron density is transferred to the area between the two carbons of the scissile bond. Such an electron density redistribution contributes to the barrier observed for these processes. Considering the electron apportionment[12] to the fragments, two modes of mesolytic scission are possible: the homolytic mode where the charge density is largely localized on the same set of atoms before and after the scission (eq 1a) and the heterolytic mode where the spin density is similarly "regioconserved" (eq 1b).

$$^{\bullet-}A{-}B \rightarrow A^{-} + B^{\bullet} \tag{1a}$$

$$^{\bullet-}A{-}B \rightarrow A^{\bullet} + B^{-} \tag{1b}$$

We describe here the fragmentation of C−C bonds in radical anions of nitro compounds where the homolytic mode of cleavage is followed (eq 1a). As we have shown before,[9c] this fragmentation mode exhibits an unexpectedly large charge delocalization in the transition state (TS). To keep the extent of such delocalization constant, in this study the electronic nature of the radical fragment was effectively fixed, but the homolytic bond strengths of the scissile bond were varied by adjusting the steric strain present in the molecule.[13] This strategy results in the adjustment of the driving force for the reaction, without affecting the charge delocalization in the transition state, and therefore allowing for a quantitative comparison with the homolysis of the same bonds in neutral substrates (Scheme 1).

Scheme 1



$1^{\bullet-}$

a: $R_1 = R_2 = Me$
b: $R_1 = (CH_2)_5 = R_2$
c: $R_1 = Me$, $R_2 = Et$ (erythro)
d: $R_1 = Me$, $R_2 = Pr$ (erythro)
e: $R_1 = Me$, $R_2 = iBu$ (erythro)
f: $R_1 = R_2 = Et$
g: $R_1 = R_2 = Bu$
h: $R_1 = R_2 = Pr$
i: $R_1 = Me$, $R_2 = iPr$ (threo)
j: $R_1 = Me$, $R_2 = iPr$ (erythro)

Results

The radical anions of **1a**−**j** were produced by one-electron reduction of the neutral substrates using reducing agents such as Li^+ 2,4,6-tri-*tert*-butylnitrobenzenide[14] (Li^+ $TTNB^{\bullet-}$) or Li^+, Na^+, or K^+ 1-(dimethylamino)naphthalenide[15] (Li^+, Na^+, or K^+ $DMAN^{\bullet-}$). The radical anions were examined by ESR, UV/vis, and cyclic voltammetry (CV). For reasons of experimental convenience, the most extensive set of data was obtained for lithium salts in Me_2SO, but a similar behavior was observed for different counterions, or in other polar solvents (DMF, CH_3CN).

In all cases the unpaired electron was strongly localized on the nitrophenyl moiety. The radical anions showed indistinguishable ESR spectra nearly identical to that observed for *tert*-butylnitrobenzene radical anion. In Me_2SO, the spectra displayed 27-peak patterns with a large coupling constant to a nitrogen nucleus ($a_N = 10.15 \pm 0.05$ G) and two sets of smaller coupling constants to *ortho* and *meta* protons ($a_{H_o} = 3.30 \pm 0.05$ G, $a_{H_m} = 1.10 \pm 0.05$ G). The UV/vis spectra of all radical anions also showed great similarity to each other and to that of *tert*-butylnitrobenzenide (in Me_2SO: $\epsilon_{333} \approx 8400$ M^{-1} cm^{-1} and $\epsilon_{462} \approx 1400$ M^{-1} cm^{-1}). In Me_2SO/0.1 M $Me_4N^+ClO_4^-$ at 25 °C, the reductions of **1a**−**j** showed reversible CV waves in the −1.05 to −1.10 V range (vs SCE) at scan rates as slow as 20−100 mV/s.

The radical ions decayed with rates dependent on the steric crowding. The least strained $\mathbf{1a}^{\bullet-}$ decayed with a measurable rate only at elevated temperatures. The decay observed in the 80−125 °C range was, however, *second order* in the concentration of $\mathbf{1a}^{\bullet-}$. No fragmentation products have been detected in this case, and the corresponding amine (in the molar amount corresponding to one-sixth of the initial molar quantity of radical anion) was recovered in addition to the unreacted **1a**. Essentially identical behavior was observed for $\mathbf{1b}^{\bullet-}$.

In the same temperature range, the sterically more crowded $\mathbf{1c}^{\bullet-}$ underwent both cleavage (ca. 60% of the decay) and reduction. The activation parameters for cleavage of $\mathbf{1c}^{\bullet-}$ were obtained after the correction based on the apparent second-order rate, measured for $\mathbf{1a}^{\bullet-}$ under the same conditions of temperature and concentration, was applied to the data. This correction assumes that the reduction rate is independent of the substitution of the benzylic carbons. The corrected rate constants were then used to construct the Eyring plot. Both the rate and the activation parameters obtained for this compound have to be considered as being only approximate.

All other radical anions in the series underwent exclusively the C−C bond fragmentation. The decays of $\mathbf{1d}$−$\mathbf{j}^{\bullet-}$ followed the first-order kinetics up to 4 half-lives. Only the products resulting from the scission of the central C−C bond were detected (see below). The rate constants presented in Table 1 were obtained by ESR. The rates and free energies of activations obtained by UV/vis or CV were very similar to the ESR data. The kinetics of the reactions was probed[9c] more extensively with $\mathbf{1f}^{\bullet-}$. No significant counterion effects on rates were detected in Me_2SO. The rate of cleavage was independent of the concentration of the radical anion (in the 0.0005−0.02

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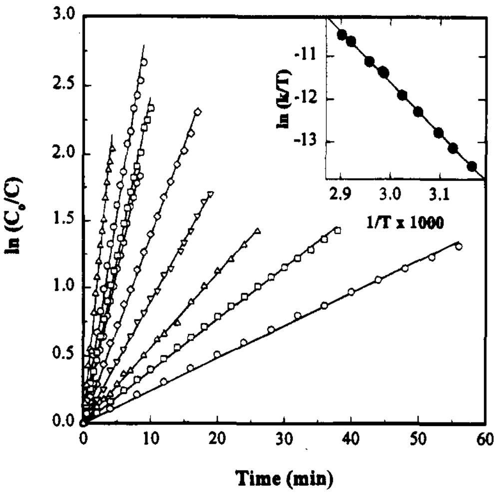

Figure 1. The first-order kinetics of the decay of Li$^+$ **1e**$^{\bullet-}$ in Me$_2$SO at different temperatures, as measured by ESR. The inset shows the Eyring plot obtained for this derivative (for clarity the highest temperature data of the Eyring plot are not included in the decay plot). The lines represent linear least-squares fits of the data.

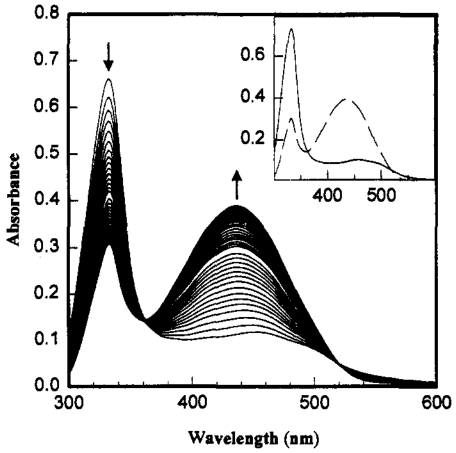

Figure 2. UV/visible spectra of the decay of Li$^+$ **1f**$^{\bullet-}$ in Me$_2$SO at ambient temperature. The inset shows a spectrum of the *p-tert*-butylnitrobenzene radical anion (solid line) prepared by reduction of the neutral with Li$^+$ TTNB$^{\bullet-}$ and the 3-(*p*-nitrophenyl)-3-pentyl anion (broken line) prepared by proton abstraction from the corresponding hydrocarbon. The spectra were taken at ca. 15-s intervals. The initial concentration of the radical anion was ca. 8 × 10^{-5} M.

M range) and of concentration of the neutral (in the 0.0005−0.05 M range). The decay rates measured in the presence of a small excess of Li$^+$TTNB$^{\bullet-}$ (1.5−2 equiv) were within experimental error (20%) of those measured under conditions when ≤1.0 equiv of this reducing agent was used. The kinetics of the decay of **1f**−**j**$^{\bullet-}$ was followed over a 40 degree temperature range centered around 30 °C. In the case of **1d**$^{\bullet-}$ the temperature range was 75−105 °C, and for **1e**$^{\bullet-}$ it was 40−75 °C. The rates measured at multiple temperatures (from 7 to 15 independent measurements) were used to construct Eyring plots and to determine the activation parameters (Figure 1).

The primary observed products of these cleavages were the corresponding α,α-dialkyl-*p*-nitrobenzyl anions as illustrated in the UV/vis experiment (Figure 2). The identity of the anions was confirmed by the independent generation of these species by proton abstraction from the corresponding benzylic hydrocarbons with the dimsyl anion ($\epsilon_{333} \approx 3800$ M^{-1} cm^{-1}, $\epsilon_{436} \approx 4900$ M^{-1} cm^{-1}). The clear isosbestic points together with the established extinction coefficients imply a clean 1:1 conversion of the radical anions into the benzylic anions with the concomitant productions of the benzylic radicals (not directly observed). Similarly, the carbanions were detected in the CV experiments carried out at higher temperatures (irreversible oxidation waves with peak potentials at 100 mV/s at ca. −0.30 to −0.35 V vs SCE).

The reversibility of cleavage was tested with stereochemically pure (*erythro* or *threo*) samples of **1e**, **1i**, and **1j**. The fragmentation reaction of the Li$^+$ salts of radical anions was carried out in Me$_2$SO to ca. 60−70% conversion, and the remaining starting materials were recovered and tested for stereochemical purity. In no case was there any stereochemical scrambling observed (≥1% would be detected).

In several cases, the preparative scale experiments were carried out to identify the ultimate products.[9c] The fragments observed were dependent on the workup procedure. Under strictly deoxygenated conditions, quenching with MeOH gave the *p*-nitro-α,α-dialkyltoluenes. If the oxygen was present, the carbanionic fragments yielded the corresponding benzyl alcohols or ketones (loss of one alkyl group). The radical fragments underwent reduction only if the initial concentration of the radical anions was high (>0.01 M). The resulting carbanionic fragments then yielded corresponding hydrocarbons or alcohols. More commonly, the radical fragments underwent coupling to yield tetramers with the undetermined structure.[9c]

For comparison, the homolysis of the neutrals was also investigated. The pyrolysis of **1a**,**e**,**f**,**j** was carried out in sealed capillaries in xylene or decaline with a large excess of thiophenol as a radical scavenger. The disappearance of the starting materials was followed by GC or HPLC. The fragments observed were the corresponding α,α-dialkyltoluenes. The sample of **1e** recovered from the pyrolysis reaction run at 160 °C to 65% conversion showed no *threo* isomer present (≤1%), by comparison with the authentic sample. Thus, the homolysis was shown to be irreversible under the conditions employed.[16] Kinetic data at three or four different temperatures covering the 40 °C range were used to construct the Eyring plots. The activation parameters obtained were very similar to those obtained by Rüchardt[13] for the analogous compounds without the nitro group. Indeed, a linear correlation was observed for the free energy of homolysis ($\Delta G^{\ddagger}_{\mathrm{h}}$ calculated at 300 K) between the data for nitro compounds and the corresponding unsubstituted analogues ($\Delta G^{\ddagger}_{\mathrm{h}}(\mathrm{NO_2}) = 1.12\Delta G^{\ddagger}_{\mathrm{h}}(\mathrm{H}) - 3.8$ (in kcal/mol); $r^2 = 0.99$). This correlation was used to calculate the free energies of homolysis of the remaining nitro compounds which were not pyrolyzed in our laboratory (Table 1).

Discussion

The crowding of the alkyl groups in **1a**−**j** (and the corresponding hydrocarbons) introduces strain in the center of the molecule. This strain may be estimated by the methods of molecular mechanics,[13d] or by the comparison of the experimental heats of formation[13c] with those calculated for nonstrained (hypothetical) molecules using, for example, Benson's group additivity.[17] The resulting strain energies obtained for the hydrocarbons[13] are collected in Table 1. The strain directly

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(16) Stereochemistry scrambling (*threo* $\rightharpoonup$ *erythro*) requires relative rotation of benzylic fragments (radicals of ions) in the solvent cage. Lack of detectable scrambling indicates that cage escape (or reactions with scavengers constituting part of the cage) is faster than such a rotation. Bond reformation without stereochemical scrambling is not detected.

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Table 1. Kinetic Data for Homolysis and Mesolysis of Nitrophenylphenylethanes (**1a**–**j**)

		homolysis[b]			mesolysis[c]			
	H_s[a]	$\Delta H^\ddagger_h$	$\Delta S^\ddagger_h$	$\Delta G^\ddagger_h$	k_m	$\Delta H^\ddagger_m$	$\Delta S^\ddagger_m$	$\Delta G^\ddagger_m$
1a	11.9	49.7	21	43.4	*d*			≥30.0
		46.0	*14*	*41.7*				
1b	13.2			(42.6)	*d*			
		47.6	*18*	*42.2*				
1c	15.1			(42.0)	4.4×10^{-8}	28.4	1	28.0
		48.4	*24*	*41.2*				
1d	14.2			(40.3)	1.0×10^{-7}	28.3	6	26.5
		45.6	*21*	*39.2*				
1e	18.7	44.1	30	35.0	2.0×10^{-5}	24.0	2	23.5
		40.4	*18*	*35.0*				
1f	27.4	45.6	37	34.5	6.3×10^{-4}	22.4	3	21.4
		41.9	*26*	*34.0*		14.8	−21	21.1[f]
		44.7	*34*	*34.5*[e]		[16.1]	[−17]	[21.2][f]
						[15.0]	[−15]	[19.5][g]
1g	22.3			(32.0)	3.1×10^{-3}	19.5	−4	20.6
		38.2	*22*	*31.6*		[13.4]	[−21]	[19.8][f]
1h	24.6	38.9	25	31.5	2.0×10^{-3}	23.7	10	20.6
		34.9	*13*	*31.0*				
1i	29.4			(30.9)	8.9×10^{-5}	25.2	9	22.5
		35.1	*14*	*30.8*				
1j	29.7	33.7	13	29.8	2.9×10^{-4}	22.1	1	21.8

[a] Strain energy in the hydrocarbon evaluated by molecular mechanics (ref 13b,d) in kcal/mol. [b] Enthalpies (in kcal/mol) and entropies (in eu) of activation for homolysis of the hydrocarbons (in italics, ref 13) and the nitro derivatives. The values in parentheses for the nitro derivatives were extrapolated from the hydrocarbon data (see text). The estimated errors of determinations for the nitro compounds are ±1 kcal/mol for enthalpies of activation and ±5 eu for activation entropies. The free-energy values are given at 300 K. [c] The rate constants (in s^{-1}, reported at 300 K) and the activation parameters for mesolytic cleavages. The enthalpies of activation (in kcal/mol) have average errors of ±0.8 kcal/mol and the entropies of activation (in eu) have errors of ±3 eu, with the exception of the data for **1c**, where the errors are larger (see text). The free energy of activation is reported at 300 K. The data in brackets were obtained by CV in the presence of 0.1 M tetraethylammonium perchlorate. [d] Second-order kinetics, the estimate of $\Delta G^\ddagger_m$ is based on the apparent activation parameters observed for the decay. [e] Two different kinetic methods gave slightly different results (ref 13b). [f] In Me_2SO containing 0.1 M Me_4NClO_4. [g] In CH_3CN containing 0.1 M Me_4NClO_4.

manifests itself by the weakening of the central, bibenzylic bond in homolysis reactions as shown in elegant studies on the hydrocarbons by Rüchardt.[13] The nitro compounds of this investigation are equally affected. Thus, the free energies of activation for homolysis of the nitro derivatives are essentially identical to those of the hydrocarbon derivatives (Table 1). The absence of significant effect of the aromatic substituents on homolysis of these compounds has been noted previously.[5b,13b]

In our homolysis studies, the enthalpies and entropies of activation are slightly higher than the corresponding values of Rüchardt.[13b] These differences may be due to the presence of the nitro group, but are more likely the result of different thermolysis conditions, or systematic errors leading to an apparent self-compensation[17] between $\Delta H^\ddagger_h$ and $T\Delta S^\ddagger_h$. Indeed, in one of the reported experiments (**1f**) run by Rüchardt[13b] with the help of a different technique and under slightly different conditions, the values of the activation parameters are essentially identical to those determined by us for the nitro compound. Regardless of their origin, these *small* discrepancies are not significant from the point of view of our studies. We conclude that free energies of activation for homolysis of the nitro derivatives can be accurately approximated by the hydrocarbon values for those cases where such data have not been obtained. Our analysis will be based mostly on the free-energy terms and thus the discrepancies will not enter into the consideration. It is worth noting here that the entropies of activation for homolysis are uniformly high (13–37 eu). Those large values are consistent with the production of fragments (14–18 eu expected for C–C bond scission[17]) and with the release of rotational degrees of freedom in those side alkyl groups that are locked in the ground state.[13b]

The strain present in these compounds is also apparent in the mesolytic reactions. The least strained radical anions ($\mathbf{1a,b}^{\bullet-}$) did not undergo scission of the C–C bond even at elevated temperatures (up to 125 °C). The observed second-order decays apparently corresponded to the rate-limiting disproportionation of the radical anion to the neutral and the dianion, followed by a rapid protonation of the later by Me_2SO or a solvent impurity (such as residual H_2O). Thus, these reactions are just examples of a well-known reduction of the nitro group to the amine.[18] From the apparent activation energy measured for $\mathbf{1a}^{\bullet-}$ ($\Delta G^\ddagger_{app}(300K) = 28$ kcal/mol) one can deduce that the undetected fragmentation reaction in this case must have $\Delta G^\ddagger_m \geq 30$ kcal/mol. Only in the slightly more strained $\mathbf{1c}^{\bullet-}$ did the fragmentation reaction start to compete with the reduction (at <110 °C).

In all other radical anions, $\mathbf{1d}$–$\mathbf{j}^{\bullet-}$, the C–C bond scission was the only reaction detected. The experiments established that the studied reaction corresponded to clean unimolecular fragmentation of the radical anion to the nitrobenzyl anion and the corresponding benzyl radical. The reaction gave good first-order kinetics up to 90% conversion, and well-defined isosbestic points (Figure 2). The ESR data showed that the unpaired electron was initially highly localized on the nitrophenyl moiety. The electron jump to the other ring prior to the bond scission was excluded by the observed activation energies. Such a jump would be energetically up hill[19] by at least 43 kcal/mol, much more than the observed $\Delta G^\ddagger_m$. The reaction was found to be irreversible. However, an "in cage" recombination of the anion and the radical without the prior rotation of one of the fragments cannot be excluded.[16] In general, the fragmentation reaction is reversible, and the barriers to radical–anion coupling are small,[5a] but under the specific reaction conditions the fragments undergo secondary reaction (such as radical–radical coupling) with small or no barrier and, therefore, no reversibility is detected. The question of apparent reversibility is of importance since the reactions under study are endergonic[5a] (see below).

The cleavage reaction is mechanistically well defined and can serve as a good model of an elementary process of radical anion fragmentation. The extra electron density is initially localized over the aromatic ring on one side of the scissile bond. The near-perfect alignment of the σ^*-orbitals of the scissile bond with both π-systems (see below for an exception) allows for "smooth" delocalization of the electron density over the entire molecule as the reaction progresses.[1,20] The electronic similarity of the departing radical fragments makes the extent of such delocalization almost constant throughout the series. Thus, the kinetics is influenced mostly by the steric and solvent effects. Those limitations make the comparison of the two modes of cleavage, homolysis and mesolysis, viable.

The solvents used for mesolytic studies were selected to minimize ion pairing or any aggregation. Indeed for $\mathbf{1f}^{\bullet-}$ in Me_2SO there was no effect of the counterion (Li^+, Na^+, K^+) on the rate of reaction,[9a] and the rate constants obtained in DMF or CH_3CN were similar to their Me_2SO counterparts. An unusual solvent effect was observed when the activation parameters were determined in the presence of 0.1 M Et_4NClO_4 serving as an electrolyte ($\mathbf{1f}^{\bullet-}$ and $\mathbf{1g}^{\bullet-}$). Although the activation energies ($\Delta G^\ddagger_m$) were identical (within experimental

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error) to those determined in the absence of the added salt, the enthalpies and entropies of activation were significantly different for the two environments. In the presence of added salt, the $\Delta H^{\ddagger}_{m}$ values decreased by 6−8 kcal/mol, but that decrease was counterbalanced by the corresponding decreases in the entropies of activation (self-compensation[21]). This effect is believed not to be an artifact of the kinetic method, but to reflect a trend that is perhaps characteristic of the mesolytic reactions. To support this conclusion we point out that the observed changes are clearly outside of the experimental error, and are not connected with the technique, time scale, or temperature range of the experiment. For instance, the activation parameters determined for **1f**$^{\bullet-}$ by ESR in Me$_2$SO in the presence of electrolyte (from 21 to 59 °C) are very similar to those determined by CV in the same solvent (from 29 to 72 °C).

Similar influence of polar additivities on the activation parameters was observed for radical cation fragmentations.[10] It possibly reflects the increased transition state stabilization by the polar additive that can be obtained only at quite specific entropy-expensive geometrical orientations of the radical ion, the solvent, and the polar additive. Whatever its origin, this self-compensation phenomenon results in a very small solvent effect on the rate of mesolytic reactions under study. As a consequence, the most meaningful comparison of mesolytic and homolytic fragmentation reaction can be obtained with free-energy values that are rather insensitive to the environmental influences. Such an analysis avoids any problems associated with a selection of particular reaction conditions that yield an apparently uncontrolled partition of activation energy into enthalpic and entropic terms.

There are some noteworthy general trends, however, that are observed for activation enthalpies and entropies of mesolytic reactions. Thus, in Me$_2$SO without added salts, in the less crowded members of the series (**1c**−**g**), the activation enthalpies of mesolysis are ca. 20 kcal/mol lower than the corresponding activation enthalpies for homolysis. That difference gradually diminishes to ca. 10 kcal/mol with the increasing strain (**1h**−**j**). The entropies of activation for mesolysis are also dramatically lower than the corresponding values for homolysis, becoming strongly negative in highly ionic media. The main contribution to the decrease in activation entropies is presumably due to the solvation of the forming benzylic anions that is hindered around the benzylic carbon by the large alkyl side groups. Another factor may involve a smaller degree of strain release in the transition state for mesolytic reactions (see below), and a concurrent smaller increase in the rotational degrees of freedom of the alkyl side chains. The average decrease in $\Delta G^{\ddagger}$ values between homolysis and mesolysis is ca. 12.5 kcal/mol (less for **1ij**). It corresponds to the bond activation obtainable by the redox process (see below).

The correlation between the ground-state strain (H_s) and the activation energy of homolysis is quite good (Figure 3) for nitro compounds with strain of up to 26 kcal/mol. Beyond that point no clear trend is observed. The slope of the correlation is near unity, indicating that release of strain provides the main impetus for the bond cleavage and that most of the strain is relieved in the transition state for homolysis. In agreement with this interpretation the intercept of the correlation is 56 kcal/mol, close to the expected value of ca. 50−57 kcal/mol for homolysis of a hypothetical strain-free 1,2-diphenylethane derivative that results in two tertiary benzylic radicals. Although no such compound exists, the appropriate independent estimate of free energy of activation for such a model can be obtained by subtracting twice the difference in C−H bond dissociation energies (assuming $\Delta\Delta S_h \approx 0$)[22] of toluene[22,23] (ΔH_h = 85−89 kcal/mol) and cumene[22,23] (ΔH_h = 83.5−84.5 kcal/mol) from $\Delta G^{\ddagger}_{h}$(300K) = 60 kcal/mol measured for bibenzyl.[24] The breakdown of the correlation for the most strained compounds is most likely the result of the incomplete release of strain in the transition state. This residual strain remains in the sterically-crowded benzylic radicals.[13b] For example, the radical derived from **1i** or **1j** has H_s of ca. 3 kcal/mol. The reasons for deviations observed for **1f** that yields almost strain-free radicals are not clear.

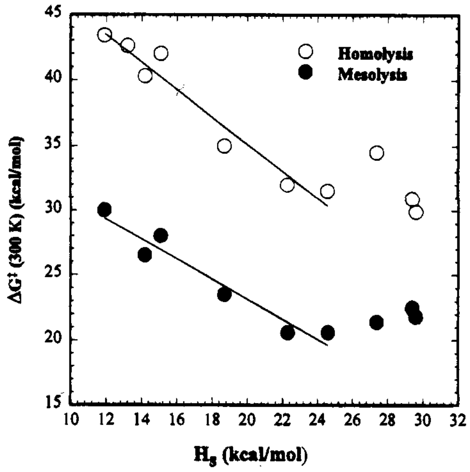

Figure 3. Plot of free energy of activation for homolysis (**1**) and mesolysis (**1**$^{\bullet-}$) as a function of strain (H_s) present in the compounds. The most strained derivatives (**f**,**i**,**j**) have been excluded from the correlations. The mesolytic data contain the estimated $\Delta G^{\ddagger}_{m}$ for **1a**$^{\bullet-}$. The correlations are as follows: $\Delta G^{\ddagger}_{h} = -1.0H_s + 55.9$ ($r^2 = 0.95$) and $\Delta G^{\ddagger}_{m} = -0.77\mathrm{H}_s + 38.6$ ($r^2 = 0.94$).

Very similar correlation is observed between H_s and the activation energy for mesolysis. Here, however, only part of the strain is released in the transition state. This is true for the most strained members of the series (H_s > 26 kcal/mol), where the benzylic radicals and anions produced are strained themself,[13b] and also for the less crowded derivatives that show a correlation slope of only 0.77. In accordance with the Hammond postulate, this trend can be related to the relatively earlier transition state (less bond elongation) for mesolysis (as compared to homolysis). As indicated above, the free energies of mesolysis are, on average, ca. 12.5 kcal/mol smaller than those of homolysis. Another explanation may involve the role of the solvent (see above) in the transition state. Even with nearly completely broken bonds the solvation of the incipient benzylic anion may

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[21] (a) Grunwald, E.; Steel, C. *J. Am. Chem. Soc.* **1995**, *117*, 5687. (b) Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; John Wiley and Sons: New York, 1963. (c) Linert, W.; Jameson, R. F. *Chem. Soc. Rev.* **1989**, *18*, 447. (d) Linert, W. *Chem. Soc. Rev.* **1994**, *23*, 429.

[22] ΔH°_{f} of toluene is 11.9−12.4 kcal/mol (ref 23a,b), ΔH°_{f} of benzyl radical is 47−49 kcal/mol (ref 23c,d,e), ΔH°_{f} of cumene is 1.0 kcal/mol (ref 23a,b), ΔH°_{f} of cumyl radical is 32.4 kcal/mol (ref 23f). All values are at 298 K. Alternatively, C−H bond dissociation energy of toluene is given as 85−89 kcal/mol (ref 23d,e,g) and that of cumene as 83.5−84.4 kcal/mol (ref 23d,g). Both these reactions have very similar ΔS° values (ref 23g).

[23] (a) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: New York, 1986. (b) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279. (c) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1989**, *17* (Suppl.), 1. (d) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. (e) Rossi, M.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1230. (f) Robaugh, D. A.; Stein, S. E. *Int. J. Chem. Kinet.* **1981**, *13*, 445. (g) Stein, S. E. *Structure and Properties*; National Institut of Standards and Technology, Standard Reference Data Program: Gaithersburg, 1994.

[24] Stein, S. E.; Robaugh, D. A.; Alfieri, A. D.; Miller, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 6567.

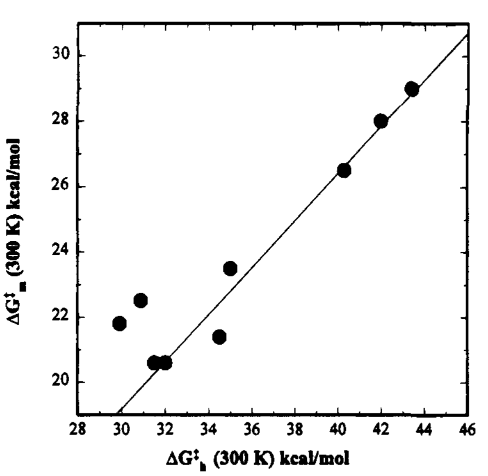

Figure 4. Correlation between the free energies of activation for homolysis and mesolysis. The data for **1i,j** have been excluded from the least-squares line ($\Delta G^{\ddagger}_{m} = 0.77\Delta G^{\ddagger}_{h} - 4.2$, $r^2 = 0.97$).

hinder the alkyl side groups. Extrapolation of the observed correlation indicate that a hypothetical strain-free radical anion would undergo scission of the C−C bond with $\Delta G^{\ddagger}_{m} = 39$ kcal/mol, a value some 17 kcal/mol lower than that expected for the corresponding homolytic process (see below).

Since both the homolysis and mesolysis show similar dependence on the strain present in the molecules, their free energies of activation show a strong correlation as well (Figure 4). The correlation becomes very good if two data points that belong to two diastereomers of the most crowded members of the series (**1i** and **1j**) are excluded from consideration. Although such an exclusion may seem arbitrary for data points that are less than 2−3 kcal/mol removed from the correlation line, we believe that this treatment is justified by similar, but even more pronounced, behavior of an analogous radical cation.[10] These observations suggest that there is an additional contribution to the barrier of the reaction in **1i,j**$^{\bullet-}$, absent in other members of the series. We propose that this contribution has stereoelectronic origins.[1,9c] X-ray structures of several derivatives of these hydrocarbons[13,20,25] showed that in all cases but one the conformation adopted by the compounds in the solid state has the dihedral angles between the scissile bonds and the aromatic planes close to 90° (average of 86°), assuring the perfect overlap between the aromatic π-system and the developing benzylic radical or ion. The exception is found for **1i** where that angle is only 74° for one of the phenyl groups.[20] The rotation barriers around the aromatic-benzylic carbon are ca. 7−14 kcal/mol in these compounds.[13a] Most likely, a part of this energy has to be expanded to bring the π-system and the scissile bond into the fuller overlap. This rotational contribution to the reaction barrier is relatively small for homolysis reactions with $\Delta G^{\ddagger}_{h}$ in excess of 30 kcal/mol, more important for radical anion cleavage with $\Delta G^{\ddagger}_{m}$ of ca. 21 kcal, and quite significant for radical cation cleavages with $\Delta G^{\ddagger}_{m}$ of under 12 kcal/mol.

Regardless of the deviations, the correlation of Figure 4 illustrates the redox activation of the C−C bond in bibenzylic systems. As mentioned above, the average difference between the free energies of activation for homolysis and mesolysis is ca. 12.5 kcal/mol (excluding **1i,j**), slightly more for the less crowded compounds and slightly less for the more-strained derivatives (the slope of the correlation is 0.77). From the thermodynamic point of view,[1,5a] the maximum activation, ΔA, is equal to the difference in the reduction potentials of the radical anion precursor ($E°_{AB}$) and the resulting nitrobenzyl radical ($E°_{A\cdot} = E°_{A^-}$). This difference[5a] ($\Delta A = 23.06\Delta E = 23.06(E°_{AB} - E°_{A\cdot})$) is ca. 16−17 kcal/mol, disregarding the small variations between the different members of the series.[5a] This estimated activation is almost equal to that extrapolated (Figure 3) for the hypothetical strain-free derivative (see above). Thus, at least for the most endergonic reactions, almost full redox activation is obtainable. Restating it in different terms, the transition state for mesolysis is lowered in energy as compared to that for homolysis by the difference in their free energies ($\Delta G^{\ddagger}_{h} - \Delta G^{\ddagger}_{m} \approx \Delta G_{h} - \Delta G_{m}$).

The data collected here provide an excellent starting point for analysis of the free-energy relationship for mesolytic reactions. Such an analysis, requiring determination of ΔG_{h} and ΔE for each member of the series, is presented elsewhere,[11] but it is already clear that the reactions presented here are endergonic ($\Delta G_{m} > 16$ kcal/mol) and that a large activation of C−C bonds observed in mesolysis (as compared to homolysis) have thermodynamic origins.

Experimental Section

^{1}H NMR spectra were taken on Bruker WP-200 (200 MHz), Bruker AM-300 (300 MHz), and Bruker AM-360 (360 MHz) instruments. ^{13}C NMR spectra were recorded on the Bruker WP-200 (50.3 MHz), Bruker AM-300 (75.5 MHz), and Bruker AM-360 (90.6 MHz) instruments. Chemical shifts are reported in ppm referenced to Me_4Si. Infrared (IR) spectra were obtained using a Perkin-Elmer Model 281 B infrared spectrometer. Unless otherwise noted all spectra were recorded from films deposited on NaCl plates from CH_2Cl_2 solution. Absorption peaks are reported in cm^{-1}. UV/visible measurements were carried out on an HP-8452A spectrophotometer. Mass spectra were taken on a Kratos MS 9/50 double focusing spectrometer in Electron Impact (EI) or Chemical Ionization (CI) mode. Only structurally significant peaks or those with a relative intensity greater than 10% of the base peak are reported. ESR spectra were recorded on a Varian E-Line spectrometer with a 9-in. water-cooled electromagnet. The microwave bridge was set at approximately 9.1 GHz. Sample temperature in the ESR cavity was controlled with a Varian variable-temperature controller. Analytical gas chromatography was carried out on a Varian 3700 gas chromatograph with a flame ionization detector, using a 50 cm × $^1/_8$ in. column packed with 5% OV-101 on 80/100 Supelcoport, and connected to a HP 3390A integrator. Preparative flash chromatography was performed with Machery Nagel silica gel 60, 230−400 mesh. Preparative HPLC was carried out on a Rainin Rabbit HP/HPX system equipped with Knauer variable-wavelength monitor, Shimadzu C-R3A Chromatopac integrator, Rheodyne 7125 sample injector, and 21.4 mm ID × 25 cm L, 8 μm-silica column using Aldrich or J. T. Baker HPLC solvents at a 22 mL/min flow rate.

Kinetic and product studies were carried out under anhydrous and anaerobic conditions. Argon was purified by passing it over an oxygen-removal catalyst (Chemalog R3-11, BASF) and a drying agent ($CaSO_4$). Anhydrous solvents (Me_2SO, DMF, CH_3CN) were obtained from Aldrich. The solvents were deoxygenated under argon by repeated freeze−pump−thaw cycles. Transfers of solutions were done with Hamilton gas-tight syringes.

2,4,6-Tri-*tert*-butylnitrobenzene radical anion (TTNB$^{\bullet-}$ Li$^+$) was prepared according to Guthrie.[14] (Dimethylamino)naphthalenide (DIMAN$^{\bullet-}$ K$^+$, DIMAN$^{\bullet-}$ Na$^+$, DIMAN$^{\bullet-}$ Li$^+$) was prepared following the procedure of Bank and Platz.[15]

UV/visible measurements and kinetic ESR studies were performed as described previously.[9c] CV data were obtained on a BAS-100A electrochemical analyzer using a variable-temperature cell. A three-electrode system was used, utilizing a Ag/AgCl reference electrode, platinum wire auxiliary electrode, and Pt working electrode. Ferrocene was employed as an internal standard. Tetraethylammonium perchlorate (0.1 M) was used as an electrolyte. The measurements were carried under argon. The compound to be studied (5−15 mg) was dissolved in 10 mL of the electrolyte and sparged with argon. Cyclic voltammograms were recorded at various scan rates at temperatures where

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[25] Littke, W.; Drück, U. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 406.

partial reversibility were observed. The rate constants were obtained from the ratio of peak currents, as described in the literature.[26]

The thermolysis was carried out in *cis*-decalin, xylenes, or a mixture of these solvents in the presence of a large excess of thiophenol (up to 20 equiv). The samples (0.008−0.01 M in **1**) containing internal standard were degassed and sealed in capillary tubes. After timed pyrolysis at preset temperatures (oil or salt bath) the samples were analyzed for disappearance of starting materials by GC or HPLC. Rates obtained at several temperatures spanning at least 40 °C were used to obtain activation parameters. Further details are provided in the following paper.[10]

The substituted bibenzyls were prepared by nitration of the corresponding hydrocarbons.[13ae,27] The hydrocarbons were treated with nitric acid in acetic anhydride[28] solution to yield mono- and bis-4-nitrophenyl derivatives which were separated by chromatography and recrystallized from absolute ethanol as described previously[9c,20] for **1f,g,i,j**. Spectral data of the remaining derivatives are given below.

2,3-Dimethyl-2-(4-nitrophenyl)-3-phenylbutane (1a): mp 113−114 °C. ^{1}H NMR (60 MHz, CDCl$_3$) 8.12 (d, J = 8.5 Hz, 2 H), 7.20 (m, 7 H), 1.46 (s, 12 H). IR 2975, 1590, 1500, 1470, 1430, 1370, 1335, 1115, 825 cm^{-1}. MS (EI), *m/e* 191 (1), 165 (27), 120 (11), 119 (100), 118 (5), 91 (30), 79 (6). MS (CI), *m/e* 284 (3), 283 (2), 282 (8), 250 (6), 249 (5), 248 (8), 205 (26), 194 (25), 193 (100).

1-(1′-Phenylcyclohexyl)-1-(4″-nitrophenyl)cyclohexane (1b): mp 155−156 °C. ^{1}H NMR (360 MHz, CDCl$_3$) 8.02 (d, J = 9 Hz, 2 H), 7.17 (m, 3 H), 7.03 (d, J = 9 Hz, 2 H), 6.87 (m, 2 H), 2.30 (m, 4 H), 1.36−1.67 (m, 10 H), 0.91−1.19 (m, 6 H). MS (EI), *m/e* 206 (13), 205 (100), 204 (11), 188 (9), 158 (22), 150 (7), 137 (41), 136 (11), 130 (6), 129 (16), 128 (7), 120 (6), 116 (14), 115 (10), 106 (8), 91 (6), 90 (12), 78 (7).

***erythro*-3,4-Dimethyl-3-(4′-nitrophenyl)-4-phenylhexane (1c):** ^{1}H NMR (200 MHz, CDCl$_3$) 8.03 (d, J = 8.5 Hz, 2 H), 7.00 (m, 7 H), 2.21 (m, 2 H), 1.57 (m, 2 H), 1.30 (s, 3 H), 1.29 (s, 3 H), 0.56 (m, 6 H). IR 2960, 2875, 2780, 1610, 1515, 1475, 1435, 1370, 1330, 1195, 1150, 1105, 1040, 1005, 980, 925, 790, 675. MS (EI), *m/e* 231 (20), 179 (14), 174 (6), 148 (5), 133 (65), 132 (8), 118 (6), 117 (13), 115 (11), 105 (19), 103 (7), 92 (9), 91 (100), 78 (6), 77 (9), 57 (30), 55 (24).

***erythro*-4,5-Dimethyl-4-(4′-nitrophenyl)-5-phenyloctane (1d):** mp 60−63 °C. ^{1}H NMR (CDCl$_3$, 200 MHz) 8.02 (d, J = 9 Hz, 2 H), 7.22 (m, 3 H), 7.02 (d, J = 9 Hz, 2 H), 6.88 (m, 2 H), 2.09 (m, 2 H), 1.60 (m, 2 H), 1.34 (s, 3 H), 1.27 (s, 3 H), 1.10 (m, 2 H), 0.80 (m, 6 H), 0.75 (m, 2 H). MS (CI), *m/e* 340 (4), 284 (15), 236 (23), 234 (14), 194 (100), 147 (56), 105 (29), 91 (14). IR (KBr) 3052, 2961, 2876, 1601, 1516, 1478, 1348, 1098, 849, 775, 704.

***erythro*-2,4,5,7-Tetramethyl-4-(4′-nitrophenyl)-5-phenyloctane (1e):** ^{1}H NMR (360 MHz, CDCl$_3$) 7.96 (d, J = 9 Hz, 2 H), 7.15 (m, 3 H), 7.00 (m, 2 H), 6.87 (m, 2 H), 2.07 (m, 2 H), 1.57 (m, 1 H), 1.45 (m, 1 H), 1.37 (s, 3 H), 1.29 (s, 3 H), 1.18 (m, 2 H), 0.85 (m, 6 H), 0.61 (d, J = 7.5 Hz, 3 H), 0.54 (d, J = 7.5 Hz, 3 H). IR 3080, 3050, 2990, 2940, 2850, 1730, 1600, 1510, 1460, 1330, 1090, 835, 745, 755, 715, 685. MS (EI), *m/e* 252 (1), 207 (6), 161 (7), 151 (6), 119 (4), 118 (7), 117 (5), 106 (9), 105 (100), 91 (15). MS (CI), *m/e* 413 (1), 366 (100), 326 (32), 310 (27), 308 (30), 208 (49), 207 (29), 206 (59), 149 (23).

4,5-Dipropyl-4-(4′-nitrophenyl)-5-phenyloctane (1h): mp 84−85 °C. ^{1}H NMR (200 MHz, CDCl$_3$) 7.96 (d, J = 9.0 Hz, 2 H), 7.14 (m, 3 H), 7.02 (d, J = 9.0 Hz, 2 H), 6.87 (m, 2 H), 1.74−2.07 (m, 8 H), 0.92−1.20 (m, 8 H), 0.77−0.92 (m, 12 H). MS (EI), *m/e* 368 (4), 350 (2), 324 (2), 305 (2), 279 (1), 221 (11), 175 (23), 136 (11), 133 (24), 131 (2), 119 (28), 118 (24), 117 (14), 115 (12), 105 (25), 91 (100).

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