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RELATIVE HOMOLYTIC STRENGTHS OF N—H BONDS IN CYCLIC AND ACYCLIC DIACYLHYDRAZIDES, IMIDES AND HYDRAZOIC ACID

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With the aid of a thermochemical cycle consisting of acidity and new redox data in dimethyl sulfoxide (DMSO) solution, homolytic N—H bond dissociation energies (ΔBDE values) relative to acetamide (1) (where the N—H BDE for 1 is defined as 0 kcal mol^{-1}) were determined for diacetamide (0), biuret (+1), 3,3-dimethylglutarimide (−3), diacetylhydrazine (−16), 4,4-dimethylpyrazolidine-3,5-dione (−25), 4-dimethylurazole (−29), hydrazoic acid (−15), succinimide (−15) and 1,2-dimethylurazole (−13) (all values in kcal mol^{-1}). These ΔBDE data provide (a) additional evidence for the minimal N—H bond weakening effects of adjacent carbonyl groups, (b) evidence for relatively large N—H bond weakening effects of adjacent —NHC(O)R moieties in both cyclic and acyclic hydrazides and (c) evidence suggesting that urazolyl radicals are more stable than pyrazolidinedionyl radicals, relative to their hydrogenated precursors. Inserting the appropriate acidity and redox data for hydrazoic acid into a thermochemical cycle that includes a constant that permits comparison of DMSO solution BDEs with gas-phase BDEs yields estimates of 93 kcal mol^{-1} for the homolytic strengths of the N—H bonds present in succinimide and H—N_3. The DMSO N—H BDE determined in this way for H—N_3 is in remarkable agreement with a determination of its gas-phase value, whereas the DMSO N—H BDE for succinimide places it intermediate between three published estimates of its gas-phase value.

INTRODUCTION

Organic radicals in which unpaired electron density formally resides on divalent nitrogen are an important class of reactive intermediates. One of the more direct ways of evaluating the stabilities and reactivities of nitrogen-centered radicals is to examine the energetics of various N—H bond homolyses. Published gas-phase N—H bond-strength data include homolytic enthalpic bond dissociation energies (BDEs) for H_2N—H (107 kcal mol^{-1}), H_3CNH—H (100 kcal mol^{-1}), $(H_3C)_2N$—H (92 kcal mol^{-1}), F_2N—H (76 kcal mol^{-1}) and C_6H_5NH—H (88 kcal mol^{-1}) (1 kcal = 4·184 kJ). That N—H bond strengths are comparable to C—H bond strengths can be inferred from comparing the aforementioned N—H BDEs with gas-phase C—H BDEs for H_3C—H (105 kcal mol^{-1}), H_3CCH_2—H (101 kcal mol^{-1}), $(H_3C)_2CH$—H (99 kcal mol^{-1}) and $C_6H_5CH_2$—H (88 kcal mol^{-1}). On the other hand, whereas a pair of α-F substituents weaken the N—H bond in H_2N—H by *ca* 30 kcal mol^{-1}, C—H BDE data for F_2CH—H (101 kcal mol^{-1}) indicate that similar replacement of hydrogen with fluorine weakens the C—H bond in H_3C—H by only 4 kcal mol^{-1} (the uncertainty in most gas-phase homolytic BDEs is *ca* 2 kcal mol^{-1}).

Among the most studied of all nitrogen-centered radicals are imidyl[2] and hydrazyl[3] radicals. Despite the voluminous literature associated with the chemistry of imidyl and hydrazyl radicals, little is known about the homolytic strengths of N—H bonds present in the parent imides. Recently, Bordwell[4] determined N—H BDEs [in dimethyl sulfoxide (DMSO) solution] for the appropriate bonds present in several acyl- and sulfonylhydrazides [DMSO solution BDEs for hydrazyl N—H bonds present in hydrazides G—$NHNH_2$ and G′—$NHN(CH_3)_2$, including G=$CH_3C(O)$—, PhC(O)— and $PhSO_2$— (82, 81 and 81 kcal mol^{-1}, respectively) and G′=PhC(O)— and $PhSO_2$— (82 and 80 kcal mol^{-1}, respectively), are given in Ref. 4]. This paper describes the results of our investigations of the DMSO solution homolytic strengths of (imide) N—H bonds in diacetamide, 3,3-dimethylglutarimide, succinimide, 1,2-dimethylurazole, and related imides, (hydrazyl) N—H bonds in diacetylhydrazine, 4,4-dimethylpyrazolidine-3,5-dione, 4-dimethylurazole,

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and related diacylhydrazides and the N—H bond in H—N_3 (hydrazoic acid). The relative homolytic bond strengths for these species were evaluated with the aid of thermochemical cycles.

RESULTS AND DISCUSSION

The use of thermochemical cycles consisting of acid–base and redox data permitted straightforward comparisons of the homolytic strengths of chemical bonds present in several varieties of solution phase organic molecules.[4,5] As shown in the equation

$$\Delta BDE(N—H) = 1{\cdot}37\Delta pK_a(N—H) + 23{\cdot}06\Delta E_{ox}(N^-) \quad (1)$$

relative homolytic bond dissociation energies (ΔBDEs) for labile N—H bonds can be obtained by comparing (a) the N—H equilibrium acidities for the species at hand and (b) the E_{ox} values for the conjugate bases (N^-) derived from the relevant nitrogen acids. It has been demonstrated empirically that relative BDEs obtained via equation (1) can be converted into 'absolute' BDEs that agree with gas-phase enthalpic BDEs if a constant (*ca* 56 kcal mol^{-1}) is added to its right-hand side, in both aqueous[6a] and DMSO[6b] solution.

Acidity and redox data necessary to evaluate the relative homolytic strengths of N—H bonds present in seven imides, nine diacylhydrazides, hydrazoic acid, and acetamide are listed in Table 1. All of the data in Table 1 were collected in DMSO solution. Inspection of the data reveals that the N—H BDEs for acetamide and diacetamide are approximately equal. These data provide further confirmation of the minimal effect that adjacent carbonyl groups have on the homolytic strengths of N—H bonds, since Bordwell *et al.*[11] have shown that the solution-phase N—H BDE for acetamide is approximately equal to the gas-phase N—H BDE for ammonia. Mindful of the fact that the ΔBDEs in Table 1 reflect changes in both the stability of the 'nitrogen acid' (N—H) and the incipient nitrogen-centered radical (N·) derived from the nitrogen acid, it seems likely that the stabilization afforded N· by adjacent carbonyl groups is offset by the stabilization afforded N—H by the same carbonyl moieties, in both acetamide (**1**) and diacetamide (**2**). ΔBDE data for biuret (**3**) indicate a minimal bond strengthening effect due to the

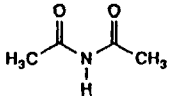
Table 1. DMSO solution pK_a values (25 °C) and relative acidity constants (ΔpK_a) for substrates **1–18**, oxidation potentials [$E_{ox(n-H^+)}$] and relative oxidation potentials (ΔE_{ox}) for the conjugate bases derived from substrates **1–18** and relative N—H homolytic bond dissociation energies (ΔBDE) for **1–18**

Substrate (*n*)	pK^{aa}	ΔpK_a[b] (kcal mol^{-1})	$E_{ox(n-H^+)}$[c] (V)	ΔE_{ox}[d] (kcal mol^{-1})	ΔBDE[e] (kcal mol^{-1})
Acetamide (**1**)	25·5[4]	(0·0)	0·73[4]	(0·0)	(0·0)
Diacetamide (**2**)	17·9[7]	−10·8	1·18	+10·4	0
Biuret (**3**)	20·1	−7·8	1·11	+8·8	+1
3,3-Dimethylglutarimide (**4**)	17·3[7]	−11·6	1·12	+9·0	−3
Diacetylhydrazine (**5**)	16·7[8]	−12·1	0·56	−3·9	−16
Dibenzoylhydrazine (**6**)	13·6	−16·3	0·65	−1·8	−18
4,4-Dimethylpyrazolidine-3,5-dione (**7**)	13·5[8]	−16·4	0·36	−8·5	−25
4-Dimethylurazole (**8**)	12·3[8,9]	−18·1	0·27	−10·6	−29
4-Phenylurazole (**9**)	11·0[8,9]	−19·9	0·34	−9·0	−29
4-(4-Methoxyphenyl)urazole (**10**)	11·4[8]	−19·3	0·31	−9·7	−29
4-(4-Methylphenyl)urazole (**11**)	11·3[8]	−19·5	0·32	−9·5	−29
4-(3-Chlorophenyl)urazole (**12**)	10·4[8]	−20·7	0·40	−7·6	−28
4-(4-Chlorophenyl)urazole (**13**)	10·6[8]	−20·4	0·36	−8·5	−29
Hydrazoic acid (**14**)	7·9[10]	−24·5	1·14	+9·4	−15
Succinimide (**15**)	14·7[10]	−15·2	0·74	+0·2	−15
Hydantoin (**16**)	15·0[8,9]	−14·8	0·74	+0·2	−15
1-Methylhydantoin (**17**)	14·7[10]	−15·2	0·73	0·0	−15
1,2-Dimethylurazole (**18**)	12·3[8,9]	−18·4	0·96	+5·3	−13

[a] References for the acidity data, if published previously, are given.
[b] At 25 °C, 1 pK_a unit is equal to 1·37 kcal mol^{-1}. Therefore, for a given substrate *n*, where *n* possesses two acidic protons, ΔpK_a (kcal mol^{-1}) = 1·37[$pK_{a(n)}$ − 25·5], where 25·5 is the pK_a for acetamide in DMSO solution. If *n* possesses one acidic proton, ΔpK_a (kcal mol^{-1}) = 1·37[$pK_{a(n)}$ − 25·8]. Negative ΔpK_a values signify that the molecule in question is a stronger acid than acetamide.
[c] For electrochemistry conditions, see Experimental. The $E_{ox(n-H^+)}$ value for acetamide is taken from Ref. 4.
[d] At 25 °C, 1 V is equal to 23·06 kcal mol^{-1}. For the anion derived from a given substrate *n*, ΔE_{ox}(kcal mol^{-1}) = 23·06[$E_{ox(n-H^+)}$ − 0·73], where 0·73 is the E_{ox} value for the anion derived from acetamide in DMSO solution. Negative ΔE_{ox} values signify that the anion in question is easier to oxidize than the conjugate base derived from acetamide.
[e] ΔBDE values were determined with the aid of equation (1). Positive ΔBDE values signify that the bond in question is stronger than the analogous bond in acetamide.

replacement of H_3C— in **2** with H_2N—; slightly larger bond strengthening effects result when H_3C— in $H_3CC(O)NH_2$ and $H_3CC(S)NH_2$ is replaced with H_2N—.[11] The pK_a and, to a lesser extent, the ΔBDE data are therefore consistent in suggesting that electron-donating substituents G, when present as in G—C(O)NH_2, act to strengthen (in both heterolytic and homolytic senses) the amide N—H bond.

Further inspection of the data in Table 1 reveals that cyclization of diacetamide (**2**), forming 3,3-dimethylglutarimide (**4**), results in 3 kcal mol^{-1} weakening of the imide N—H bond. Effects of this magnitude are not surprising in the light of similarly small changes in C—H BDEs (<3 kcal mol^{-1}) for the following acyclic–cyclic pairs of molecules: dimethyl malonate–Meldrum's acid, pentane-2,4-dione–dimedone and pentan-3-one–cyclopentanone.[12]



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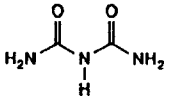

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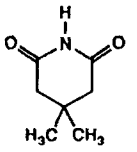

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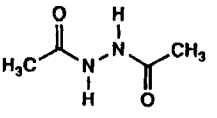
Diacylhydrazine N—H bond strengths

Arylhydrazyl radicals are among the most widely studied of all organic radicals, in part due to their remarkable persistence.[3] Bordwell[4] has determined that the α-amino substituents in $H_3CC(O)NHNH_2$ and $PhSO_2NHNH_2$ weaken (in a homolytic sense) the N—H bonds in the parent amides $H_3CC(O)NH_2$ and $PhSO_2NH_2$ by *ca* 25 kcal mol^{-1}, a difference that, from a thermodynamic perspective, certainly accounts for a good portion of the kinetic stability exhibited by hydrazyl radicals. In order for a given hydrazyl radical to display *kinetic* stability (i.e. persistence), the radical must possess (a) substantial delocalization of the unpaired electron, (b) steric congestion in the vicinity of the unpaired electron and (c) substitution appropriate to prohibit disproportionation.[13] In elegant studies, Pirkle and Gravel[14] examined the chemistry of diacylhydrazyl radicals derived from urazoles and pyrazolidine-3,5-diones. Urazolyl radicals possessing 1-α-cumyl and 1-*tert*-butyl substituents were isolated, and as such were the first hydrazyl radicals to be isolated in which the hydrazyl nitrogens lack a directly bonded aromatic group. The isolation of the appropriately substituted urazolyl radicals indicates that radicals derived from selected urazoles can be classified as persistent hydrazyl radicals. Analysis of the homolytic strengths of N—H bonds found in variously substituted urazoles with the aid of equation (1) thus seemed feasible, since the demonstrated persistence of selected urazolyl radicals seems likely to result in near optimum cyclic voltammetric (CV) oxidations of the respective urazolide anions. In addition, DMSO acidity data for the urazoles and related species are readily accessible.[8,9]

Acidity and redox data in Table 1 allow the determination of the ΔBDE data for diacetylhydrazine (**5**), dibenzoylhydrazine (**6**), 4,4-dimethylpyrazolidine-3,5-dione (**7**) and 4-dimethylurazole (**8**). Inspection of the ΔBDE data for diacetylhydrazine reveals that the adjacent —$NHC(O)CH_3$ moiety weakens the N—H bond in acetamide by about 16 kcal mol^{-1}, a result in sharp contrast to the near-zero bond weakening effect due to —$C(O)CH_3$ (i.e. diacetamide ΔBDE = 0). ΔBDE for dibenzoylhydrazine (−18 kcal mol^{-1}) is of a similar magnitude to that of diacetylhydrazine. The —$NHC(O)CH_3$ and —NHC(O)Ph substituents thus have large bond-weakening effects on adjacent N—H bonds, in both heterolytic and homolytic reactions.



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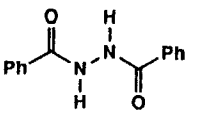

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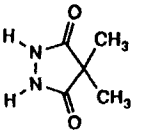

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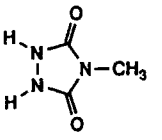

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Further inspection of the ΔBDE data in Table 1 reveals that (a) the N—H bond in 4,4-dimethylpyrazolidine-3,5-dione (**7**) is about 9 kcal mol^{-1} weaker than the N—H bond in diacetylhydrazine (**5**) and (b) the N—H bond in 4-dimethylurazole (**8**) is about 4 kcal mol^{-1} weaker than the N—H bond in 4,4-dimethylpyrazolidine-3,5-dione (**7**). The ΔBDE data for diacetylhydrazine (**5**), 4,4-dimethylpyrazolidine-3,5-dione (**7**) and 4-dimethylurazole (**8**), and the inferences (these inferences assume that the changes in the N—H BDEs for **5**, **7** and **8** are due mainly to changes in the stabilities of the radicals **5** − H·, **7** − H· and **8** − H·) that can be drawn from these data (i.e. that **8** − H· is more stable than **7** − H· and that **7** − H· is more stable than **5** − H·) are supported by spectroscopic and kinetic analyses of these and related species. First, EPR spectra for urazolyl radicals indicate that the unpaired electron is delocalized over the entire heterocycle.[14] Evidently, the cyclic nature of the urazoles forces the two acyl groups into a coplanar relationship that facilitates delocalization of the unpaired electron over the entire heterocycle. On the other hand, it is likely that the

p-orbitals located on the adjacent nitrogens in diacetylhydrazine are not coplanar, since NMR data for 1,2-dibenzyl-1,2-methoxycarbonylhydrazine indicate an orthogonal relationship between the two acyl groups in this species.[15] Second, EPR spectra for pyrazolidinedione radicals indicate that the unpaired spin density is present mainly on the hydrazyl nitrogens.[14] Finally, α-cumylpyrazolidinedione radicals have been observed to be less persistent than α-cumylurazole radicals, an effect ascribed to the presence of the imide nitrogen in the urazoles.[14]

The fact that the ΔBDE data for diacetylhydrazine (**5**), 4,4-dimethylpyrazolidine-3,5-dione (**7**) and 4-dimethylurazole (**8**) confirm previous assertions[14] regarding the relative stabilities of the radicals derived from these species attests to the viability of homolytic bond strength evaluations via equation (1).

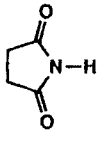
EPR spectra[14] also indicate that unpaired spin density is not appreciably delocalized into the N-4 phenyl of the 1,4-diphenylurazolyl radical. It is therefore not unexpected that there is essentially no change in the N—H BDEs for the five variously substituted 4-arylurazoles **9–13**: the 4-Cl, 3-Cl, 4-CH_3 and 4-CH_3O substituents have minimal interaction with the unpaired electron (Table 1).

Hydrazoic acid, succinimide and hydantoin imide N—H bond strengths

Also listed in Table 1 are acidity and redox data necessary to determine the ΔBDE (in DMSO) for the N—H bond in H—N_3, relative to acetamide. The data suggest that the N—H bond in H—N_3 is about 14 kcal mol^{-1} weaker than the N—H bond in acetamide. With the incorporation of the 56 kcal mol^{-1} constant in the right hand side of equation (1), it can be estimated that the 'absolute' DMSO solution BDE for H—N_3 is 93 kcal mol^{-1}, a value in remarkable agreement with a determination of the gas-phase BDE for H—N_3 (92 ± 5 kcal mol^{-1})[16] [the N—H BDE in H—N_3 was previously determined to be 79·4 kcal mol^{-1} (Ref. 17)]. Also listed in Table 1 are acidity and redox data that allow ΔBDE determinations for succinimide (**15**), hydantoin (**16**), 1-methylhydantoin (**17**) and 1,2-dimethylurazole (**18**) (−15, −15, −15 and −13 kcal mol^{-1}, respectively). That the imide N—H bond in succinimide is *ca* 10 kcal mol^{-1} stronger than a hydrazyl N—H bond in 4,4-dimethylpyrazolidine-3,5-dione (**7**) is not surprising in light of the apparent localization of the unpaired spin density (*ca* 60%) on the ^{14}N imide nitrogen in **15** − H·, the succinimidyl radical.[18] On the other hand, the data suggest that the imide N—H bonds in **15–18** are *ca* 12–15 kcal mol^{-1} weaker than the imide N-H bonds in diacetamide (**2**) and 3,3-dimethylglutarimide (**4**).

The observed 10 kcal mol^{-1} difference in N—H BDEs for 4,4-dimethylpyrazolidine-3,5-dione (**7**) and succinimide (**15**) is well outside the estimated uncertainty in each value (estimated to be ±2 kcal mol^{-1}, see Experimental). Differences in the N—H homolytic bond strengths for succinimide (and also 16–18) and 3,3-dimethylglutarimide are perplexing, and are probably best rationalized by invoking a stereoelectronic effect associated with the five-membered heterocycles **15–18**. It is important to note that the ΔpK_a data for diacetamide (**2**), 3,3-dimethylglutarimide (**4**) and succinimide (**15**) (−10·8, −11·6 and −15·2, respectively) indicate a moderate heterolytic N—H bond-weakening effect when comparing the five-membered heterocycle **15** with the larger cyclic [3,3-dimethylglutarimide (**4**)] and acyclic [diacetamide (**2**)] imidyl relatives. We are currently examining the structures and energetics of various amides, imides and their corresponding anions and radicals via *ab initio* techniques. These studies are aimed at attaining a greater understanding of the relative heterolytic and homolytic N—H bond strengths in species such as **7**, **15** and **16–18**.

The succinimide ΔBDE data are especially interesting in the light of previous estimates of the resonance energy and stability of the succinimidyl radical. On the basis of the observed 22 kcal mol^{-1} bond-weakening effect of two RC(O) groups on the O—O bond strength in H_2O_2, Walling[19] estimated that the resonance energy of the succinimidyl radical is greater than 17 kcal mol^{-1}. In arguments based in part on the expectation that the BDE for the N—N bond in the succinimide dimer (i.e. a pair of succinimidyl radicals bound at N) should be 0 kcal mol^{-1}, Dauben and McCoy[20] estimated that the resonance energy of the succinimidyl radical is *ca* 30 kcal/mol^{-1}. On the other hand, Hedaya *et al.*[2b] observed that the succinimide dimer was recovered unchanged after (a) treatment (in a sealed tube) for 24 h at 400–500 °C, (b) treatment for 48 h at 230 °C while refluxing in a 3:1 mixture of diphenyl ether and tetralin and (c) treatment for 40 h in



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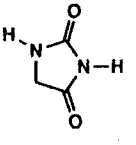

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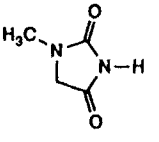

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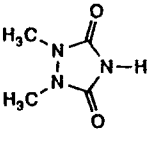

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refluxing chlorobenzene in the presence of excess of bromine. Therefore, they estimated that the N—N BDE in the succinimide dimer is about 60 kcal mol^{-1} and that the N—H BDE in succinimide is about 100 kcal mol^{-1}.

The acidity and redox data for succinimide listed in Table 1, combined with the use of the 56 kcal mol^{-1} constant in equation (1),[6b] yield an estimate of 93 kcal mol^{-1} for the N—H BDE for succinimide (**15**). As always, the irreversible nature of the oxidation potential for the succinimide nitranion demands caution in the interpretation of the ΔBDE data. Nevertheless, the demonstrated usefulness of equation (1)[5a,6] and related cycles[2] combined with the constancy in the imide N—H ΔBDE data for succinimide (**15**), hydantoin (**16**), 1-methylhydantoin (**17**) and 1,2-dimethylurazole (**18**) provide support for the listed values.

CONCLUSIONS

The data presented in this paper suggest that (a) there are similarities in the stabilities of the radicals derived from diacetamide and acetamide (**2** − H· and **1** − H·, respectively), relative to diacetamide and acetamide (**2** and **1**, respectively); (b) cyclization to six-membered heterocycles has little effect on the heterolytic and homolytic strengths of imide N—H bonds (i.e. diacetamide and 3,3-dimethylglutarimide ΔBDE values are within 3 kcal mol^{-1} of each other); (c) cyclization to five-membered heterocycles weakens both the heterolytic and homolytic strengths of imide N—H bonds, since the ΔBDE value for succinimide is 15 kcal mol^{-1} more negative than that for diacetamide; (d) adjacent —NHC(O)R moieties (as in diacetylhydrazine) weaken N—H bonds by *ca* 15 kcal mol^{-1}; (e) radicals derived from cyclic diacylhydrazines are more stable than those derived from acyclic diacylhydrazines, relative to their hydrogenated precursors; and (f) urazolyl radicals are more stable than pyrazolidinedionyl radicals, relative to their hydrogenated precursors. Points (e) and (f) are in agreement with spectroscopic and kinetic data published by Pirkle and Gravel.[14]

EXPERIMENTAL

Substrates **1**–**6** and **15**–**17** are all commercially available (Aldrich) and were crystallized to literature melting points prior to use. Potassium azide (**14** − H^+) was purchased from Aldrich and used as received. The syntheses of **7**–**12** and **18** were described previously.[8]

Dimethyl sulfoxide was purified and potassium dimsylate was synthesized as described by Matthews *et al.*[22] $Et_4N^+BF_4^-$ was recrystallized from acetone and was allowed to dry at 110 °C under vacuum prior to dissolution in DMSO.

All of the pK_a values in Table 1 have been published previously (references for these values are listed in Table 1), except for biuret (**3**) and dibenzoylhydrazine (**6**). The method used to determine the pK_a values for **3** and **6** was identical with that described previously.[9a,22] Biuret was equilibrated vs 9-benzylfluorene ($pK_{HA} = 21.4$)[10] and carbazole ($pK_{HA} = 19{\cdot}9$),[10] whereas dibenzoylhydrazine was equilibrated vs 9-fluorenone-4-chlorophenylhydrazone ($pK_{HA} = 14{\cdot}15$)[10] and 9-fluorenone-2,4-dichlorophenylhydrazone ($pK_{HA} = 11{\cdot}98$).[10] Standard deviations within a run (each consisting of at least three titration points) were generally less than 0·06 p*K* unit.

Dimethyl sulfoxide electrochemistry: 0·1 M $Et_4N^+BF_4^-$ electrolyte; Pt working and Ag/AgI reference electrodes [ferrocene/ferrocenium = +0·875 V (vs Ag/AgI) as internal standard, values corrected to NHE_{aq} by subtracting 0·125 V] (the conversion of redox data collected using an Ag/AgI reference electrode into data that are relative to NHE_{aq} has been described previously[5b,5c,12]). In the argonated electrochemical cell, the nitranions were present in 1–2 mM concentrations, with the exception of the succinimide nitration. The CV wave for the succinimide nitranion was not fully resolved at 1–2 mM concentration; therefore, higher concentrations (*ca* 5 mM) were employed for this species. The E_{ox} values in Table 1 are the anodic peak potentials for the irreversible oxidations of anions derived from **2**–**18**, as reported by a BAS 100A electrochemical analyzer, and are the averages of several runs for each compound. The reproducibilities of the E_{ox} values are ⩽25 mV (*ca* 0·5 kcal mol^{-1}). The uncertainties in the pK_a values (±0·1 pK_a unit) in Table 1, combined with the irreproducibilities and irreversible nature of the E_{ox} values in Table 1, suggest overall uncertainties in the ΔBDE values of *ca* 2 kcal/mol^{-1}.[5a,6]

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