Oxide Radical Anion Reactivity with Aliphatic Amino Compounds in Aqueous Solution: Comparison of H−Atom Abstraction from C−H and N−H Groups by $^•O^-$ and $^•OH$ Radicals

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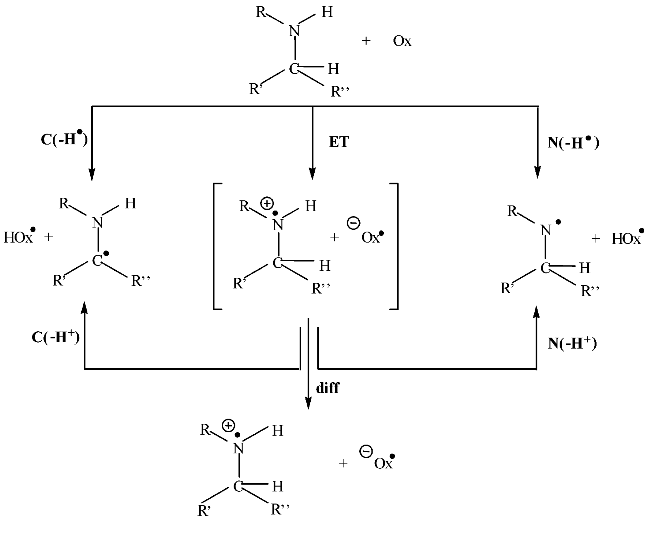
One-electron oxidants react with $H_2N-CHRR'$ amino compounds by electron transfer (ET), and direct H abstraction from N−H and C−H, giving respectively, aminium ($^{+•}NH_2CHRR'$), aminyl ($^•NH-CHRR'$), and α-C-centered radicals (H_2N-$^•CRR'$). The yields of these species from $^•O^-$ reactions with the anions of glycine (Gly$^-$), alanine (Ala$^-$), and α-methylalanine (MeAla$^-$) and with methylamine (MeNH$_2$) have been investigated at pH ≥ 13. The results indicate an ET process is negligible. Aminyl and α-C-centered radicals appear to be formed only by direct H abstraction reactions. In line with this, the ratios of the overall rates of H abstraction from N−H and C−H, $k_{N(-H^•)}/k_{C(-H^•)}$, for $^•O^-$ reacting with different amino compounds decrease with C−H bond dissociation enthalpy (BDE) and thus follow the pattern expected for direct abstraction reactions. In contrast to $^•O^-$, the conjugate $^•OH$ radical produces significant yields of aminium radicals by ET, which evidently contribute to aminyl radical formation by subsequent proton loss from nitrogen. Thus, the $k_{N(-H^•)}/k_{C(-H^•)}$ ratios for $^•OH$ are higher than those for $^•O^-$ and do not decrease regularly with C−H BDE. Formation of α-C-centered radicals via ET and subsequent proton loss from a C−H group of the aminium radical is much less likely. The overall rates of H abstraction from C−H sites by both $^•OH$ and $^•O^-$ are found to increase with the exothermicity of the reaction. Because of its spherical symmetry the steric factors for $^•O^-$ reactions are larger than those for $^•OH$, but in most cases this appears to be compensated by more favorable potential energy surfaces stemming from the 36 kJ mol^{-1} greater exothermicity of $^•OH$ reactions. $^•O^-$ reactions with charged species are of course also susceptible to the effects of Coulombic interactions.

Introduction

The oxidation of amino compounds is of importance and interest in many biological and industrial systems. The action of amine oxidases, for example, plays a key role in biochemistry and pharmacology.[1,2] Furthermore, studies of the oxidation of amines by triplet excited states of ketones and other photosensitizers have provided important information on the basic mechanism of electron transfer and the dynamics of the elementary liquid-phase reactions involved.[3] Scheme 1 shows a general mechanism for the oxidation of a primary or secondary amine by a one-electron oxidant, Ox. Specifically, the oxidant may act by electron transfer (ET) yielding an N-centered radical cation, or by direct H atom abstraction from the α-C atom, reaction C(−H$^•$), or the N atom, reaction N(−H$^•$). The time for outward diffusion from the initial encounter cage can be long enough that the same two H atom deficient products may be formed by proton transfer from the α-C or N atom of the radical cation to Ox$^{•-}$ while in proximity (reactions C(−H$^+$) and N(−H$^+$), respectively). The rates of the various processes in Scheme 1 vary, depending on the structures and $E°$ values of the amine and Ox. The reactions, which occur with tertiary amines, are similar, except that reactions N(−H$^•$) and N(−H$^+$) are absent. Also, amines carrying only tertiary alkyl groups cannot form α-amino-C-centered radicals, i.e., in this case reactions C(−H$^•$) and C(−H$^+$) are absent.

SCHEME 1



Our own interest lies in the reactions of $^•OH$ and other small water-derived radicals with aliphatic amines,[4,5] amino acids,[6−9] and peptides. In recent studies, it was shown[6−9] that $^•OH$ radicals react with amino acid anions by both the ET mechanism and H atom abstraction from N and C atoms. For example, for glycine the radicals formed are: aminium ($^{+•}NH_2-CH_2-CO_2^-$) (**1**), α-amino-α-carboxy-C-centered ($NH_2-^•CH-CO_2^-$) (**2**), and aminyl ($^•NH-CH_2-CO_2^-$) (**3**). A significant fraction of the aminium radicals, formed as part of the initial successor pair in

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reaction 1, undergo very fast decarboxylation ($k_2 \approx 10^{11}$ s^{-1}).[6,8] Reaction 2 yields the aminomethyl radical (**4**).

$$H_2N{-}CH_2{-}CO_2^- + {}^{\bullet}OH \rightarrow [OH^- \ldots {}^{+\bullet}NH_2{-}CH_2{-}CO_2^-] \quad (1)$$

$$[OH^- \ldots {}^{+\bullet}NH_2{-}CH_2{-}CO_2^-] \rightarrow OH^- + {}^{\bullet}CH_2{-}NH_2\ (\mathbf{4}) + CO_2 \quad (2)$$

This competes with proton transfer in the solvent cage which leaves the aminyl radical (**3**) (reaction N($-$H$^+$)), and possibly also some α-amino-α-carboxylmethyl radicals (**2**) (reaction C($-$H$^+$)). It is not yet known what fractions of radicals **2** and **3** are generated via the electron−proton-transfer sequence and direct H-abstraction. However, the total primary yields of radicals **2**, **3**, and **4** from the overall reactions 1a, 3, and 4, occurring within the solvent caged primary ${}^{\bullet}$OH-glycine anion interaction complex, are 37%, 36%, and 22%, respectively.[9]

$$H_2N{-}CH_2{-}CO_2^- + {}^{\bullet}OH \rightarrow OH^- + {}^{\bullet}CH_2{-}NH_2 + CO_2 \quad (1a)$$

$$H_2N{-}CH_2{-}CO_2^- + {}^{\bullet}OH \rightarrow NH_2{-}{}^{\bullet}CH{-}CO_2^- + H_2O \quad (3)$$

$$H_2N{-}CH_2{-}CO_2^- + {}^{\bullet}OH \rightarrow {}^{\bullet}NH{-}CH_2{-}CO_2^- + H_2O \quad (4)$$

These are referred to as the amine primary radical yields. Similar yields have been found for methyl-substituted glycines[9] and methylamine.[5] The identities of the primary glycine-derived radicals have been confirmed by other researchers through direct detection in time-resolved esr experiments.[10]

The current recognition of the role of ${}^{\bullet}$OH and related reactive oxygen species (ROS) in oxidative damage to living tissue,[11] is a direct indication of the relevance of such studies in biology and medicine. The results are also of practical interest in relation to the degradation of amino-containing organic complexants in nuclear-waste storage tanks.[12] The aqueous medium in these tanks is often strongly basic. It was, therefore, of interest to extend the investigations on the oxidation of amino model substances to higher pHs, i.e., to conditions where the hydroxyl radical exists in its deprotonated form ${}^{\bullet}O^-$, pK_a(${}^{\bullet}$OH/${}^{\bullet}O^-$) = 11.9.[13]

The reactions of amines with ${}^{\bullet}O^-$ are also of interest for fundamental reasons. The oxide radical anion is known to be a much less potent electron accepting species than ${}^{\bullet}$OH. It is similarly efficient though in H atom abstraction,[14] but little is known about its selectivity for attack at different sites, such as C−H and N−H. Information in the literature allows one to estimate a value of 1.1 V for $E°({}^{\bullet}O^-/O^{2-})$.[15] This is much lower than that of $E°(HO^{\bullet}/HO^-) = 1.9$ V,[19] and the ET oxidation process in Scheme 1 would clearly be much slower for the former. In fact, given that the values of $E°({}^{+\bullet}NH_2{-}CH_2{-}CO_2^-/NH_2{-}CH_2{-}CO_2^-)$[20] and $E°({}^{+\bullet}NH_2CH_2R/NH_2CH_2R)$[21] for primary amines lie in the range 1.3−1.6 V, one would expect that ET from them toward ${}^{\bullet}O^-$ should be negligible. Under those circumstances, it might be possible to observe the pure competition between the two H$^{\bullet}$ abstraction reactions without contributions from ET followed by the C($-$H$^+$) and N($-$H$^+$) processes in Scheme 1. The work we present here was undertaken with the objective of identifying the primary products of the oxide radical anion reaction with glycine anion (Gly$^-$), alanine (Ala$^-$), α-methylalanine (MeAla$^-$), and methylamine (MeNH$_2$). The study also includes a comparison of rate constants for H atom abstraction by ${}^{\bullet}O^-$ and ${}^{\bullet}$OH from the α-amino-C−H position in glycine and other C−H containing substances, so that the effects of reactant charge and other parameters could be examined. Differences in the C($-$H$^{\bullet}$) and N($-$H$^{\bullet}$) processes for ${}^{\bullet}O^-$ and ${}^{\bullet}$OH are also considered.

Experimental Section

Experimental Procedures. All investigations have been conducted in aqueous solutions with water purified by the Serv-A-Pure Co. system. Methylamine (Aldrich, 40 wt % solution in water), glycine, alanine, 2-aminoisobutiric acid (MeAla), and other chemicals (Aldrich, Fluka) were used as received from the vendors.

Pulse radiolysis was performed with an 8 MeV Titan Beta model TBS-8/16−1S LINAC at the Notre Dame Radiation Laboratory with pulses of 2.5 ns duration, and doses per pulse in the range of 2−10 Gy. A description of the pulse radiolysis setup, data collection, and processing can be found elsewhere.[22] All solutions were freshly prepared just before each experiment. They were ≥0.1 M in OH$^-$ (adjusted by NaOH), were deoxygenated (by bubbling with N$_2$), and subsequently were saturated with N$_2$O. In such systems, ${}^{\bullet}O^-$ radicals are formed according to the processes described by eqs 5−8.

$$H_2O \rightsquigarrow e_{aq}^-, {}^{\bullet}OH, H^{\bullet}, H_2, H_2O_2, H_{aq}^+ \quad (5)$$

$$H^{\bullet} + OH^- \rightarrow e_{aq}^- + H_2O \quad (6)$$

$$e_{aq}^- + N_2O + H_2O \rightarrow {}^{\bullet}OH + OH^- + N_2 \quad (7)$$

$${}^{\bullet}OH + OH^- \rightleftharpoons {}^{\bullet}O^- + H_2O \quad (8)$$

The yield of scavengable oxide radical anions, $G({}^{\bullet}O^-)$ in μmol J^{-1}, was recognized to be dependent on the scavenging capacity in each solution (concentration multiplied by the rate constant for reaction of the substrate with ${}^{\bullet}O^-$) as generally known for primary water radiolysis products.[23] Therefore, it was calculated for each system applying the formula recommended for ${}^{\bullet}$OH radicals.[24] Because it is quite low, the commonly accepted yield of $G(H^{\bullet}) = 0.06$ μmol J^{-1} [13] was used throughout the study, independent of the solute concentrations. The rate constant for reaction 6 is 2.2×10^7 M^{-1} s^{-1} [14] and those for the competing H$^{\bullet}$ reactions with the amino acids used here are taken from ref 9. The respective value for MeAla$^-$ is $<1 \times 10^7$ M^{-1} s^{-1}. In this system all H$^{\bullet}$ will exclusively react with OH$^-$ leaving ${}^{\bullet}O^-$ as the only primary reactive species available for reaction with this amino acid. The other amino acids, when present in higher concentrations, may scavenge H atoms prior to their conversion into ${}^{\bullet}O^-$. The fate of H$^{\bullet}$ in each system is clearly indicated in the text.

The total concentration of ${}^{\bullet}O^-$ radicals per pulse applied in the present investigation of N$_2$O-saturated systems varied from 1 to 6 μM. Dosimetry was performed with thiocyanate solutions as described earlier.[25] As is usual in radiation chemical experiments, the accuracy of radical yields and reaction rate constant determinations are considered to be about ±10%. This applies also to our present set of data. Error limits given for the specific numerical values refer only to the standard deviation of the mean of a series of single measurements. Experiments have been conducted at room temperature (296 ± 2 K).

Determination of Radical Yields. The radicals of the amino compounds studied here cannot be identified directly by their optical absorption spectra, because characteristics of their absorptions are not known and the λ_{max} lie far in the UV region (<300 nm). Therefore, their yields have been determined by the selective redox scavenger method described previously in related studies.[6,9] Here we briefly repeat only those features relevant to this study. The reactions for amino acid radicals of type **2**, **3**, and **4** are generic and equations are thus given only for those of Gly.

The reducing α-amino-α-carboxy-C-centered (**2**) and the α-aminomethyl radicals (**4**) were determined with the dication of methyl viologen (MV^{2+}, $E° = -0.45$ V for $MV^{2+}/MV^{\bullet+}$ couple),[19] with which they react at practically diffusion-controlled rates in reactions 9 and 10, respectively.[6,9]

$$MV^{2+} + NH_2{-}{}^{\bullet}CH{-}CO_2^- \ (\mathbf{2}) \rightarrow MV^{\bullet+} + NH{=}CH{-}CO_2^- + H^+ \quad (9)$$

$$MV^{2+} + {}^{\bullet}CH_2NH_2 \ (\mathbf{4}) \rightarrow MV^{\bullet+} + NH{=}CH_2 + H^+ \quad (10)$$

The concentration of MV^{2+} was kept to ≤0.5 mM, which ensures quantitative scavenging of **2** and **4**, but minimizes direct reduction of MV^{2+} by hydrated electrons. The latter reaction is in competition with reaction 7. The respective rate constants are available in ref 14. Formation of $MV^{\bullet+}$ was kinetically traced and the amount quantitatively determined by its absorption at 600 nm ($\epsilon_{600} = 12\,820$ M^{-1} cm^{-1}).[6]

4-Carboxybenzophenone (CB^-, $E°(CB^-/{}^{\bullet}CB^{2-}) = -1.13$ V)[26] was used to differentiate between radicals **2** and **4**. The highly stabilized α-amino-α-carboxyalkyl radical (**2**) does not react with CB^- at a measurable rate. The rate constants for reaction with α-aminoalkyl radicals (like **4** in reaction 11), on the other hand,

$$CB^- + {}^{\bullet}CH_2NH_2 \rightarrow {}^{\bullet}CB^{2-} + NH{=}CH_2 + H^+ \quad (11)$$

are large, e.g., for ${}^{\bullet}CH_2NH_2$ $k_{11} = 3 \times 10^8$ M^{-1} s^{-1}.[8] Formation of ${}^{\bullet}CB^{2-}$ was kinetically traced and the yield determined at 660 nm ($\epsilon_{660} = 7660$ M^{-1} cm^{-1}).[26]

The aminyl radicals, which are inherently oxidizing, were determined by their reaction with hydroquinone (H_2Q, $E°(Q^{\bullet-}/Q^{2-}) = 0.023$ V)[27] as described in our previous studies.[6,9] The yield of semiquinone radical anions, $Q^{\bullet-}$, formed upon one-electron oxidation of hydroquinone, was measured at $\lambda_{max} = 427$ nm ($\epsilon = 7200$ M^{-1} cm^{-1}).[28,29] Two secondary reactions of aminyl radicals, namely, β-elimination of ${}^{\bullet}CO_2^-$, reaction 12, and formation of radical **2** by H atom donation from the parent amino compound ($NH_2{-}CH_2{-}CO_2^-$) in reaction 13[7] are also of importance here.

$$ {}^{\bullet}NH{-}CH_2{-}CO_2^- \rightarrow CH_2{=}NH + {}^{\bullet}CO_2^- \quad (12)$$

$$ {}^{\bullet}NH{-}CH_2{-}CO_2^- + NH_2{-}CH_2{-}CO_2^- \rightarrow NH_2{-}CH_2{-}CO_2^- + NH_2{-}{}^{\bullet}CH{-}CO_2^- \quad (13)$$

The ${}^{\bullet}CO_2^-$ reduces both MV^{2+} and CB^- (reactions 14 and 15)

$$MV^{2+} + {}^{\bullet}CO_2^- \rightarrow MV^{\bullet+} + CO_2 \quad (14)$$

$$CB^- + {}^{\bullet}CO_2^- \rightarrow {}^{\bullet}CB^{2-} + CO_2 \quad (15)$$

while $NH_2{-}{}^{\bullet}CH{-}CO_2^-$ reacts only with MV^{2+} (reaction 9). The rates of reactions 12 and 13 are independent of the concentrations of MV^{2+} or CB^- under the conditions applied. Both occur on a time scale that is much longer than those of reactions 9−11. Therefore, the reduction of MV^{2+} and CB^- by the products of the aminyl radical decay appear as secondary growth in the kinetic traces, well separated in time from the much faster reductions by radicals **2** and **4**. In many instances the yields of aminyl radical **3** can be determined from the same traces as radicals **2** and **4**. The absolute rate constants for the type-12 reactions are as follows: 1.2×10^3 s^{-1} for Gly^-, 2.3×10^4 s^{-1} for Ala^-, and 7.3×10^4 s^{-1} for $MeAla^-$. The relatively large values for Ala^- and $MeAla^-$ make the measurement of ${}^{\bullet}CB^{2-}$ from the analogous processes to reactions 12 and 15 the preferred method for the determination of the aminyl radical yields from these amino acids.

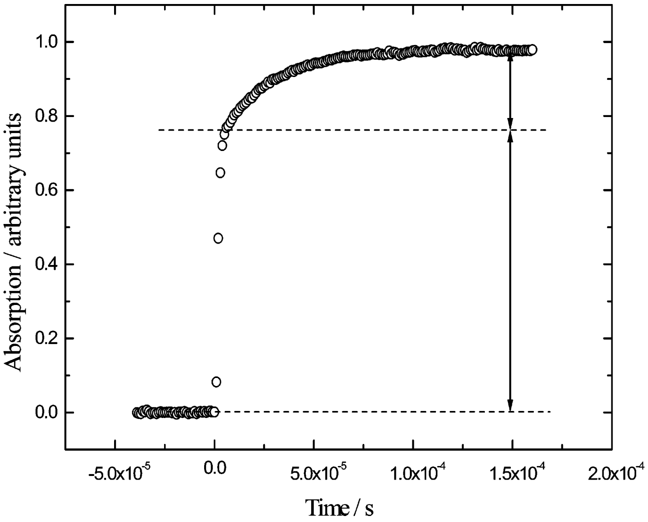

Figure 1. Absorption−time trace obtained at 600 nm in pulse irradiated N_2O-saturated aqueous solution containing 1 M glycine, 0.2 M NaOH, and 0.5 mM MV^{2+}. Dose per pulse ca. 4 Gy.

Experiments were performed with solutions containing 0.1 or 0.2 M NaOH, i.e., at pH ≥ 13, to avoid significant contributions from ${}^{\bullet}OH$ reactions. Concentrations of OH^- were, however, kept below 1 M to prevent significant hydrolysis of solutes. Given that the p*K*a of ${}^{\bullet}OH$ may even be somewhat lower than the generally accepted 11.9, viz. 11.54,[30] no more than 10% of the reactions would be due to ${}^{\bullet}OH$ in any system. Evidence that ${}^{\bullet}OH$ contributions were negligible under the conditions used also came from the failure to detect radical **4**, a specific and characteristic product of the aminium radical decay (see further below).

Results

Glycine. Oxide radical anions react with Gly^- in 1 M NaOH solutions with $k = 5.6 \times 10^8$ M^{-1} s^{-1}.[31] By analogy with the ${}^{\bullet}OH$ system, the overall reactions that might occur are

$${}^{\bullet}O^- + H_2N{-}CH_2{-}CO_2^- \rightarrow [O^{2-}...{}^{+\bullet}NH_2{-}CH_2{-}CO_2^-] \rightarrow O^{2-} + NH_2{-}{}^{\bullet}CH_2 \ (\mathbf{4}) + CO_2 \quad (16)$$

$$\rightarrow NH_2{-}{}^{\bullet}CH{-}CO_2^- \ (\mathbf{2}) + OH^- \quad (17)$$

$$\rightarrow {}^{\bullet}NH{-}CH_2{-}CO_2^- \ (\mathbf{3}) + OH^- \quad (18)$$

Yields of the resulting primary radicals **2**, **3**, and **4** were measured by pulse irradiation of a solution containing 1 M Gly, 0.2 M NaOH, and MV^{2+} in concentrations varying from 0.1 to 0.5 mM. A typical signal at 600 nm is shown in Figure 1. At all methyl viologen concentrations, about 80% of the $MV^{\bullet+}$ was formed in a fast, $[MV^{2+}]$-dependent process associated with scavenging of radicals **2** and **4**. The remaining ≈20% exhibited a much slower first-order kinetic growth with $k_{obs} = (3.9 \pm 0.2) \times 10^4$ s^{-1}. Most importantly, it is independent of $[MV^{2+}]$, suggesting that the rate-determining step is not the reduction of MV^{2+} but rather the conversion of the aminyl radicals **3** via reactions 12 and 13 into reducing radicals. The calculated overall first-order rate of 3.1×10^4 s^{-1} for the present [Gly^-], based on the published rate constant, $k_{13} = 3.0 \times 10^4$ M^{-1} s^{-1},[6] is, indeed, in good agreement with the value noted above for the slow process in Figure 1.

The total yield and the yield of the slow part of $MV^{\bullet+}$ formed in the above system were obtained to be $G_{total} = 0.73 \pm 0.01$ μmol J^{-1} and $G_{slow} = 0.195 \pm 0.005$ μmol J^{-1}, respectively, independent of [MV^{2+}] above 0.2 mM.

In the present 1 M Gly^- solution H atoms from water radiolysis ($G = 0.06$ μmol J^{-1}) react quantitatively with the glycine anion, predominantly forming radical **2** (reaction 19),[9] and thus contribute only to the fast part of the $MV^{\bullet+}$ formation.

$$H^\bullet + NH_2-CH_2-CO_2^- \rightarrow NH_2-{}^\bullet CH-CO_2^- + H_2 \quad (19)$$

Therefore, the observed yield of $MV^{\bullet+}$ due to reducing radicals formed by ${}^\bullet O^-$ is equal to ($G_{total} - G_{H^\bullet}$) = 0.73−0.06 = 0.67 μmol J^{-1}. The yield of scavengable $G_{^\bullet O^-} = 0.70$ μmol J^{-1}, calculated by taking into account the scavenger capacity of Gly^- in this solution and applying the formula recommended for ${}^\bullet OH$ radicals,[24] is in good agreement with this.

The reasonable conclusion that G_{slow} for $MV^{\bullet+} = G_{(3)}$ implies that 29% (=100 × 0.195/0.67) of all oxide radical anions reacted with Gly^- by reaction 18 to form aminyl radicals. Their reaction with hydroquinone was used to analyze for these oxidizing transients in a more direct way. The observable product is the semiquinone radical formed in reaction 20. (At 0.1 M NaOH, pH ~ 13, hydroquinone is present with > 95% in its dianion form and only a minor amount in the monoprotonated HQ^- form).

$$^\bullet NH-CH_2-CO_2^- \ (\mathbf{3}) + Q^{2-} + H_2O \rightarrow Q^{\bullet -} + OH^- + H_2N-CH_2-CO_2^- \quad (20)$$

Figure 2a shows a typical absorption−time trace obtained upon pulse radiolysis of an N_2O-saturated solution containing 0.1 M Gly^-, 0.1 M NaOH, and 1 mM hydroquinone. The record was taken at 427 nm where $Q^{\bullet -}$ exhibits its absorption maximum. Immediately after the pulse a first very fast step (0.2 on the arbitrary ordinate scale) is recognized. The yield of it did not exceed 0.04 μmol J^{-1} even at the highest hydroquinone concentration employed (5 mM), and this absorbance results from the direct oxidation of hydroquinone by primary water radicals. This initial step is followed by a slower increase before the signal eventually starts to decay. The kinetics were subjected to a fitting process by applying exponential functions for both the slow growth and the early parts of the decay process, as discussed in detail previously.[6,7] The pseudo-first-order rate constants (k_{obs}) for the slow growth of the $Q^{\bullet -}$ absorption, corrected for the decay process, increased with increasing hydroquinone concentration. The plot of k_{obs} vs [Q^{2-}] in Figure 2b shows a good straight line with a slope giving $k_{20} = (1.7 \pm 0.2) \times 10^7$ M^{-1} s^{-1}. This rate constant is about four times lower than the value determined at pH 11 where hydroquinone exists mainly in the HQ^- form.[6] The observed decrease of the overall rate constant at pH 13 is expected. One reason is that the hydroquinone prevails as doubly negatively charged Q^{2-} at this pH and, accordingly, the negatively charged aminyl radical **3** faces a higher Coulombic repulsion. Furthermore, the protons necessary for reaction 20 have to come from the solvent water. In Marcus theory terms, this causes an increase in reorganization energy.[32]

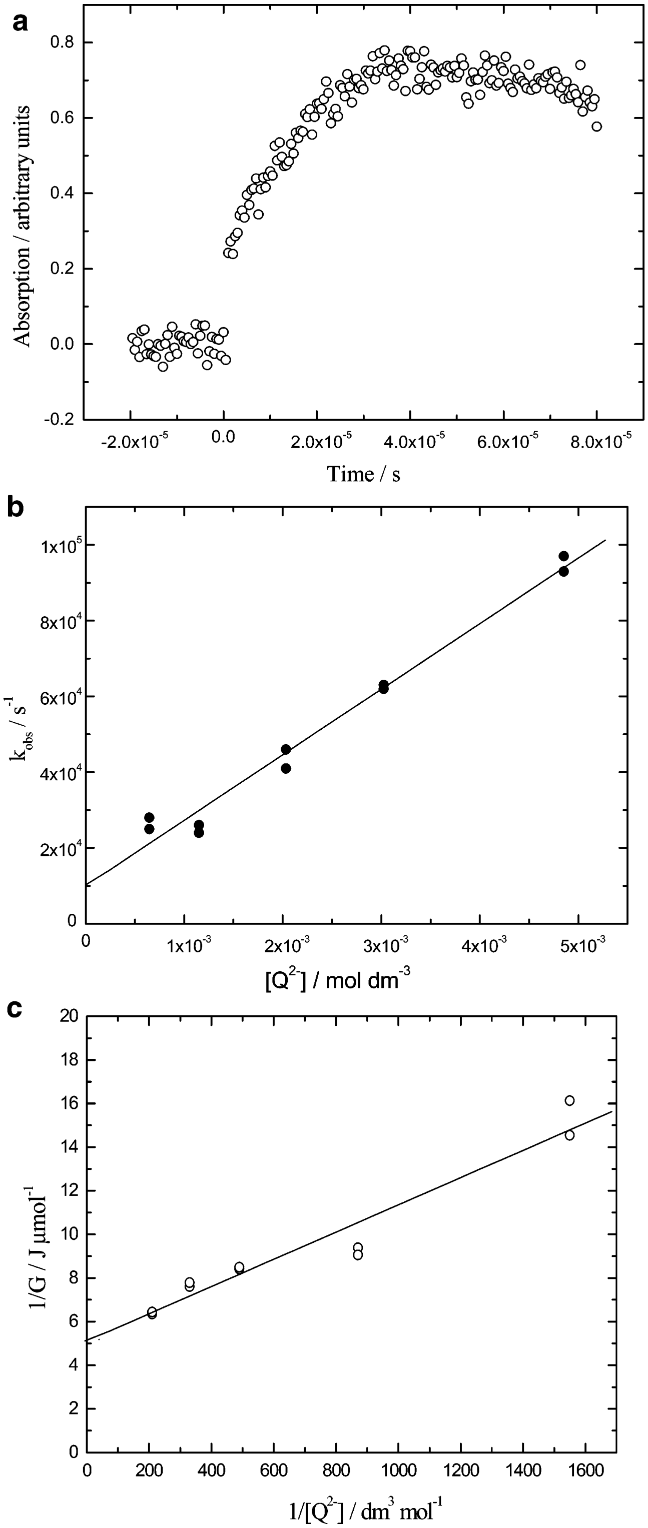

Figure 2. (a) Absorption−time trace obtained at 427 nm in pulse irradiated N_2O-saturated aqueous solution containing 0.1 M glycine, 0.1 M NaOH, and 0.1 mM hydroquinone, Q^{2-}. Dose per pulse ca. 7 Gy. (b) Plot of k_{obs} for semiquinone formation at 427 nm against Q^{2-} concentration (0.5−5 mM). (c) Reciprocal semiquinone yield against reciprocal Q^{2-} concentration for the same solutions.

Figure 2c shows a plot of $1/G(Q^{\bullet -})$ against $[Q^{2-}]^{-1}$, where $G(Q^{\bullet -})$ is the yield of the semiquinone measured at each hydroquinone concentration. This reciprocal plot was necessary, because aminyl radicals are not only removed via the relatively slow reaction 20 but competitively also via reactions 12 and 13. The absolute yield of aminyl radicals, $G_{aminyl} = 0.20 \pm 0.02$ μmol J^{-1}, has been determined from the intercept of this plot.

TABLE 1: Yields of Primary Radicals Formed upon Reaction of Oxide Radical Anion or Hydroxyl Radical with Methylamine and Aliphatic Amino Acid Anions in Aqueous Solutions, Expressed as Percentage of Attacking Radicals

	oxidizing radical ${}^{\bullet}O^-$ for primary radical		oxidizing radical ${}^{\bullet}OH^{a}$ for primary radical		
	$NH_2-{}^{\bullet}CRR'$	${}^{\bullet}NH-CHRR'$	$NH_2-{}^{\bullet}CRR'$	${}^{\bullet}NH-CHRR'$	${}^{+\bullet}NH_2-CRR'CO_2^{-b}$
CH_3NH_2	48	52	37[c]	63[c]	
Gly^-	70	30	37	36	22
$Ala^{-\,d}$	73	22	22	47	25
$MeAla^{-\,e}$		68		61	25

[a] From ref 9 unless otherwise indicated. [b] Taken as the yield of decarboxylated product, $NH_2-{}^{\bullet}CRR'$. [c] From ref 5. [d] Side chain radical yields estimated to be ≈5%. [e] Side chain radical yields: 30% and 18% for ${}^{\bullet}O^-$ and ${}^{\bullet}OH$, respectively; for ${}^{\bullet}NH-CHRR'$, read ${}^{\bullet}NH-CMeRR'$.

To compare this value with the yield determined by the MV^{2+} method, it has to be related to the yield of scavengable oxide radical anions for the 0.1 M Gly^- concentration. The latter has been calculated to be $G_{{}^{\bullet}O^-} = 0.62$ μmol J^{-1}, thus implying that 32% ($=100 \times 0.20/0.62$) of the ${}^{\bullet}O^-$ radical anions reacted with glycine anions by abstracting a hydrogen atom from the amino group. This is in very good agreement with the 29% result obtained above from the slow MV^{2+} reduction yield. Thus, one can conclude that about 30% of ${}^{\bullet}O^-$ react with Gly^- to produce aminyl radical **3**, while the remainder of 70% produce radicals which react with MV^{2+} on the fast time scale.

Attention is now turned to the question of what portion of this fast MV^{2+}-reduction yield corresponds, respectively, to radicals **2** and **4**. As indicated in the Determination of Radical Yields in the Experimental Section, this can be resolved by using CB^- as scavenger which responds only to **4** in reaction 11. Experiments were done in N_2O-saturated 0.1 M Gly with 0.5 mM CB^- and 0.1 M NaOH. At this CB^- concentration and with $k_{11} = 3 \times 10^8$ M^{-1} s^{-1},[8] the calculated half-life for CB^- reduction by ${}^{\bullet}CH_2NH_2$ is ≈5 μs. However, no ${}^{\bullet}CB^{2-}$ attributable to reaction 11 was seen on the 1−10 μs time scale. Only small absorptions, corresponding to yields of 0.02−0.04 μmol J^{-1} and attributable to the direct reaction of e_{aq}^- with CB^- occurring in competition with reaction 7, were formed in less than 1 μs ($k(e_{aq}^- + CB^-) = 2 \times 10^{10}$ M^{-1} s^{-1}).[14] One can, therefore, set the yield of the ${}^{\bullet}CH_2NH_2$ (**4**) radical and its ${}^{+\bullet}NH_2-CH_2-CO_2^-$ (**1**) ET precursor at ≤0.03 μmol J^{-1}. The fraction of ${}^{\bullet}O^-$ undergoing reaction 16 is thus ≤4% ($\leq 100 \times 0.03/0.67$). The only significant reactions of ${}^{\bullet}O^-$ with $NH_2-CH_2-CO_2^-$ are, therefore, 17 and 18, with the yields of aminyl type **3** and α-amino-α-carboxy-C-centered type **2** radicals being 30% and 70%, respectively. These and corresponding yields of primary radicals for the other systems, reported below, are given in Table 1.

Taking these yield ratios and the overall ${}^{\bullet}O^- + NH_2-CH_2-CO_2^-$ rate constant of 5.6×10^8 M^{-1} s^{-1} in 1 M NaOH solution,[31] partial rate constants, $k_{17} = 3.9 \times 10^8$ M^{-1} s^{-1} and $k_{18} = 1.7 \times 10^8$ M^{-1} s^{-1}, are evaluated. It should be recognized though that these reactions are between two negatively charged ions and the rate constants, consequently, depend on the ionic strength, μ, of the solution. The above values refer to $\mu = 1$.

The yield determination experiments with CB^-, incidentally, did not indicate any measurable yield of ${}^{\bullet}CO_2^-$ from β-fragmentation of ${}^{\bullet}NH-CH_2-CO_2^-$ (**3**), confirming the earlier pH 11 results.[7]

Alanine and α-Methylalanine. The reaction of ${}^{\bullet}O^-$ with Ala^- can produce radicals analogous to **1**, **2**, **3**, and **4**, while with $MeAla^-$ only those analogous to **1**, **3**, and **4** are in principle possible. In addition, for both of these glycine derivatives H-abstraction can also occur from the β-amino-CH_3 groups, reactions 21 and 22. However, these $-{}^{\bullet}CH_2$ radicals are unreactive toward the redox scavengers used,[9] and their formation was not explored in this investigation.

$$ {}^{\bullet}O^- + NH_2-CH(CH_3)\text{-}CO_2^- \rightarrow NH_2-CH({}^{\bullet}CH_2)\text{-}CO_2^- + OH^- \quad (21) $$

$$ {}^{\bullet}O^- + NH_2-C(CH_3)_2-CO_2^- \rightarrow NH_2-C(CH_3)({}^{\bullet}CH_2)\text{-}CO_2^- + OH^- \quad (22) $$

CB^- was employed as a scavenger for the determination of ${}^{\bullet}CO_2^-$ formed in reactions analogous to reaction 12 on the 100 μs time scale. Also from the yields formed on the 1−10 μs time scale this scavenger gives an indication of whether α-aminoalkyl radicals of type **4**, are formed. As in the case of Gly^- discussed above, the absence of any appreciable reduction of CB^- in this time domain for both Ala^- and $MeAla^-$ indicated that the yield of type **4** radical (and its type **1** precursor) was ≤0.03 μmol J^{-1} and that for practical purposes ET between ${}^{\bullet}O^-$ and these amino acid anions was negligible. The only primary radicals of interest which remain are, therefore, those from reactions 23 and 24 (Ala^-) and 25 ($MeAla^-$).

$$ {}^{\bullet}O^- + NH_2-CH(CH_3)\text{-}CO_2^- \rightarrow NH_2-{}^{\bullet}C(CH_3)\text{-}CO_2^- + OH^- \quad (23) $$

$$ {}^{\bullet}O^- + NH_2-CH(CH_3)\text{-}CO_2^- \rightarrow {}^{\bullet}NH-CH(CH_3)\text{-}CO_2^- + OH^- \quad (24) $$

$$ {}^{\bullet}O^- + NH_2-C(CH_3)_2-CO_2^- \rightarrow {}^{\bullet}NH-C(CH_3)_2-CO_2^- + OH^- \quad (25) $$

Measurements of aminyl radical yield from Ala^- via reaction 24 were made in 0.02 M Ala^- and 0.2 M NaOH solution containing 0.5 mM CB^-. The relatively low Ala^- concentration was used to ensure that the majority of aminyl radicals formed in the system would undergo β-fragmentation and liberate ${}^{\bullet}CO_2^-$ in a process analogous to reaction 12, and only a minor part would be converted into type **2** radicals inert toward CB^- via the analogoue of reaction 13.[7] From the known rate constants an overall first-order rate of 2.6×10^4 s^{-1} was estimated for the aminyl radical decay rate and the fraction forming ${}^{\bullet}CO_2^-$ was calculated to be 0.87. The yield of ${}^{\bullet}CB^{2-}$ from the optical absorption at 660 nm was equal to 0.12 μmol J^{-1}. From this $G_{\text{aminyl}} = 0.12/0.87 = 0.14$ μmol J^{-1} has been calculated. The scavengable yield of oxide radical ions, calculated assuming that the overall rate constant for its reaction with Ala^- was equal to the rate constant for Gly^- and that H atoms were reacting quantitatively with OH^- for the relatively low [Ala^-] in this system, was $G_{({}^{\bullet}O^-)\text{total}} = G_{({}^{\bullet}O^-)} + G_{{}^{\bullet}H} = 0.58 + 0.06 = 0.64$ μmol J^{-1}. Thus, from the yield of aminyl radicals relative to ${}^{\bullet}O^-$, the probability of reaction 24 and the fractional yield of aminyl radicals is 22%. In the absence of aminium radical **1** formation the remaining ${}^{\bullet}O^-$ radical anions undergo reactions 23 and 21. From experience with ${}^{\bullet}OH$ the yield of side chain radicals from the latter is expected to be only ∼5%,[9] and therefore that of the α-amino-α-carboxy-C-centerred type **2** radical can be taken as 73% (= 100−22−5).

Aqueous N_2O-saturated 0.1 M $MeAla^-$ in 0.2 M NaOH was pulse irradiated in the presence of 0.1 to 0.8 mM CB^-. Under these experimental conditions in this particular system β-fragmentation (reaction analogous to eq 12) is the only reaction the aminyl radical could undergo, and the relatively large $k_{12} = 7.3 \times 10^4\ s^{-1}$, for MeAla-derived aminyl radical causes reaction 15 to be the rate-determining step in the formation of $^{\bullet}CB^{2-}$. Thus, the $^{\bullet}CB^{2-}$ growth was pseudo-first order, the rate increasing proportionally to CB^- concentration. From the slope of the k_{obs} against $[CB^-]$ plot a second-order rate constant of $(3.3 \pm 0.2) \times 10^7\ M^{-1}\ s^{-1}$ was obtained. This matches exactly the literature value[33] of k_{15} and is, therefore, taken as evidence for $^{\bullet}CO_2{}^-$ production from aminyl radical precursor.

The yield of $^{\bullet}CB^{2-}$ at infinite CB^- concentration, which can be set equal to G_{aminyl}, was 0.45 μmol J^{-1}. The overall rate constant for the reaction of $^{\bullet}O^-$ with $MeAla^-$ is not known, but one can estimate it to be $(3 \pm 1) \times 10^8\ M^{-1}\ s^{-1}$ by taking $k_{25} \approx k_{18} = 1.7 \times 10^8\ M^{-1}\ s^{-1}$ and $k_{22} \approx 2k_{Me} = 2 \times 1.1 \times 10^8\ M^{-1}\ s^{-1}$, where k_{Me} is the partial rate constant for H abstraction from one CH_3 group in saturated alkanes.[31] This gives the yield of scavengeable $^{\bullet}O^- = 0.60\ \mu mol\ J^{-1}$ and $G_{(^{\bullet}O^-)total} = G_{(^{\bullet}O^-)} + G_{^{\bullet}H} = 0.60 + 0.06 = 0.66\ \mu mol\ J^{-1}$. The addition of 0.06 μmol J^{-1} comes again from the H atom reaction sequence 5−8. Relating now G_{aminyl} to $G_{(^{\bullet}O^-)total}$ reveals that 68% of all oxide radical ions react with $MeAla^-$ by abstracting hydrogen from the amino group, reaction 25. This large yield is consistent with the earlier esr observation of this radical at pH 13.[34] The remaining 32% of the $^{\bullet}O^-$ undergo reaction 22.

Methylamine. The overall rate constant for reaction of $^{\bullet}O^-$ with $MeNH_2$ at pH ∼ 13 has been reported to be $7.5 \times 10^9\ M^{-1}\ s^{-1}$.[35] Here, there is no experimental means of determining whether ET occurs. By analogy with the amino acid anions (see further below), it was assumed to be negligible, and the results obtained for methylamine are, therefore, interpreted only in terms of reactions 26 and 27.

$$^{\bullet}O^- + NH_2{-}CH_3 \rightarrow NH_2{-}^{\bullet}CH_2 + OH^- \qquad (26)$$

$$\rightarrow {}^{\bullet}NH{-}CH_3 + OH^- \qquad (27)$$

Hydroquinone was used for probing aminyl radical formation in reaction 27. The solution was 0.1 M in methylamine, 0.1 M in NaOH, and the hydroquinone concentration was varied in the range of 0.2 to 5 mM. The experimentally obtained traces at 427 nm were very similar to ones measured with glycine (see Figure 2a) and were evaluated the same way as described above. From the pseudo-first-order semiquinone formation rates vs $[Q^{2-}]$ plot a second-order rate constant of $k_{28} = (1.3 \pm 0.2) \times 10^7\ M^{-1}\ s^{-1}$ has been calculated. This is very similar to the rate constant for Q^{2-} oxidation by glycine aminyl radical, reaction 20, at the same pH.

$$^{\bullet}NH{-}CH_3 + Q^{2-} + H_2O \rightarrow Q^{\bullet -} + OH^- + H_2N{-}CH_3 \qquad (28)$$

However, the yield of semiquinone radicals obtained by extrapolation to infinitive hydroquinone concentration was considerably higher in the case of methylamine and amounted to $G_{aminyl} = G_{^{\bullet}Q^-} = 0.37\ \mu mol\ J^{-1}$. In relation to the yield of oxide radical anions in this system, calculated to be $G_{\bullet O^-} = 0.71\ \mu mol\ J^{-1}$, abstraction of H atom from the amine group, reaction 27, proceeds with 52% probability. In other words, in this system abstractions from N−H and C−H positions proceed with roughly equal efficiencies. From the overall rate constant, $7.5 \times 10^9\ M^{-1}\ s^{-1}$,[34] the fractional rate constants for reactions 26 and 27 are $k_{26} = 3.6 \times 10^9\ M^{-1}\ s^{-1}$ and $k_{27} = 3.9 \times 10^9\ M^{-1}\ s^{-1}$.

Discussion

The Absence of ET. The percentage yields of primary aminyl $^{\bullet}NH{-}CHRR'$ radicals, (type **3** radicals for the amino acid anions and $^{\bullet}NH{-}CH_3$ for $MeNH_2$) and the primary C-centered $NH_2{-}^{\bullet}CRR'$ radicals (α-amino-α-carboxy-C-centered type **2** species from Gly^- and Ala^-, and $H_2N{-}^{\bullet}CH_2$ radicals in the case of $MeNH_2$) determined in this study for $^{\bullet}O^-$ are given in Table 1. Also listed in this Table 1, for comparison, are the analogous yields reported earlier from overall $^{\bullet}OH$ reactions at pHs in the region 9−11. For the amino acid anions, these include the yields of type **1** $^{+\bullet}NH_2{-}CRR'{-}CO_2{}^-$ radicals which are taken as equal to the decarboxylated $NH_2{-}^{\bullet}CRR'$ radical (**4**) product yields. Since they are ≤4%, the yields of these species from $^{\bullet}O^-$ have not been listed. The absence of evidence for them means that reaction 16a and its counterparts with Ala^- and $MeAla^-$ must be insignificant.

$$^{\bullet}O^- + H_2N{-}CH_2{-}CO_2{}^- \rightarrow [O^{2-} \ldots {}^{+\bullet}NH_2{-}CH_2{-}CO_2{}^-] \qquad (16a)$$

That must also be true for ET processes where protons are drawn from neighboring solvent molecules, as in reaction 16b:

$$H_2N{-}CH_2{-}CO_2{}^- + {}^{\bullet}O^- + H_2O \rightarrow [2OH^- \ldots {}^{+\bullet}NH_2{-}CH_2{-}CO_2{}^-] \qquad (16b)$$

Such reactions provide a larger driving force than applies in eq 16a, but their rates are subject to the penalty of the reorganization energy for the transfer of protons. As explained in the Introduction, the occurrence of ET with $^{\bullet}OH$ in reaction 1 is readily understood because $E°(^{\bullet}OH/OH^-)$ of 1.9 V[19] exceeds $E°(^{+\bullet}NH_2{-}CR_2{-}CO_2{}^-/NH_2{-}CR_2{-}CO_2{}^-)$ for the amino acid systems studied here by ∼0.4 V. On the other hand, $E°(^{\bullet}O^-/O^{2-})$, estimated at 1.1 V, is a few tenths of a volt too low for an exergonic process.

Although there is no direct evidence relating to primary amines like $MeNH_2$, it is highly probable that ET, while being significant for $^{\bullet}OH$, is again negligible with $^{\bullet}O^-$. That is because the $E°(^{+\bullet}NH_2R/NH_2R)$ value of ∼1.3 V for primary amines[21] also lies between those of $^{\bullet}O^-$ and $^{\bullet}OH$. Secondary and tertiary amines were not studied here, but one should note that alkyl substitution at N can substantially reduce $E°(^{+\bullet}NRR'R''/NRR'R'')$,[36] and there may be cases where ET occurs with both radicals.

Rates of C−H Abstraction; Comparison of $^{\bullet}O^-$ and $^{\bullet}OH$ Reactivity. The fractional yields of primary radicals of type **2**, $NH_2{-}^{\bullet}CRR'$, and aminyl $^{\bullet}NH{-}CHRR'$ (**3**) were used in the Results to calculate partial rate constants for the H atom abstraction from C and N sites by $^{\bullet}O^-$, reactions 17 and 18 with Gly^- and 26 and 27 with methylamine, respectively. This section is concerned with those values for the C−H position. We specifically consider $k_{17} = 3.9 \times 10^8\ M^{-1}\ s^{-1}$ for Gly^- and $k_{26} = 3.6 \times 10^9\ M^{-1}\ s^{-1}$ for $MeNH_2$ and compare these with analogous rate constants of $^{\bullet}OH$. Also, an attempt will be made to understand the H-abstraction reactivity of both $^{\bullet}O^-$ and $^{\bullet}OH$ in more general terms by comparing their reactions with the presently investigated amino compounds to those of a series of related anionic and uncharged compounds (see Table 2).

TABLE 2: Second Order Rate Constants for H Abstractions from C−H Bonds in M^{-1} s^{-1} [a] and Bond Dissociation Enthalpies (BDE) in kJ mol^{-1} at 298 K

	oxidizing radical $^{\bullet}O^-$		oxidizing radical $^{\bullet}OH$		
reactant	k	k per H	k	k per H	BDE
			Anions[b]		
$CH_3CO_2^-$	2.5×10^7	8.3×10^6	8.5×10^7	2.8×10^7	400[c]
Gly^-	1.9×10^8 [d]	9.7×10^7	1.0×10^9 (e)	5.2×10^8	363[f]
HCO_2^-	8.4×10^8	8.4×10^8	3.2×10^9	3.2×10^9	348[c]
			Neutrals		
t-BuOH	4.0×10^8	4.4×10^7	6.0×10^8	6.7×10^7	β-C−H, 423[g]
MeOH	7.5×10^8	2.5×10^8	9.7×10^8	3.2×10^8	α-C−H, 402[h]
EtOH	1.2×10^9	6.0×10^8	2.4×10^9	1.2×10^9	α-C−H, 396[i]
2-PrOH	1.2×10^9	1.2×10^9	1.9×10^9	1.9×10^9	α-C−H 393[j]
$MeNH_2$	3.6×10^9 [d]	1.2×10^9	1.3×10^9 [j]	4.4×10^8	α-C−H 393[k]

[a] From ref 14 unless otherwise indicated. [b] Anion rate constants corrected to zero ionic strength. [c] From ref 39. [d] This study as described in text. [e] From ref 9. [f] From ref 20b. [g] Value taken as the same as that for C_2H_5−H from ref 40. [h] From ref 40. [i] From ref 41. [j] From ref 5. [k] From ref 42.

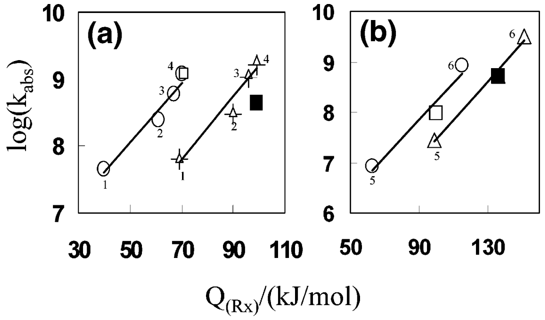

Figure 3. Logarithm of second-order rate constant for C−H abstraction per H atom vs reaction exothermicity ($Q_{(Rx)}$): (a) for neutrals and (b) for anions. H_2O-derived radical: $^{\bullet}OH$, △; $^{\bullet}O^-$, ○; Reactant: 1 = *tert*-butyl alcohol; 2 = methanol; 3 = ethanol; 4 = 2-propanol; 5 = acetate; 6 = formate. Open and filled squares: $MeNH_2$ in part a and Gly^- in part b. (Crosses in part a are for specific reactions with β-C site in *tert*-butyl alcohol and α-C elsewhere).

Partial rate constants obtained earlier for the overall C-centered radical formation by $^{\bullet}OH$ are $k_3 = 1.04 \times 10^9$ M^{-1} s^{-1} for Gly^- [9] and $k_{29} = 1.33 \times 10^9$ M^{-1} s^{-1} for $MeNH_2$.[5]

$$H_2N{-}CH_3 + {}^{\bullet}OH \rightarrow NH_2{-}{}^{\bullet}CH_2 + H_2O \qquad (29)$$

In keeping with our findings relating to the kinetic isotope effect on C−H deuteration for $MeNH_2$,[5] and because of the very low acidity (high pK_a) and kinetic rate of proton-transfer anticipated from the C−H group,[16] the contribution from the indirect electron−proton-transfer sequence for the carbon atom, process ET/C($-H^+$) in Scheme 1, is expected to be much smaller than from the ET/N($-H^+$) process. It is thus logical to treat k_3 and k_{29} as rates for the direct C($-H^{\bullet}$) processes; the same applies to k_{17} and k_{26}. In Table 2, these partial rate constants are listed along with rate constants for H atom abstraction from C−H sites for other compounds, which are charged (for comparisons with Gly^-) or neutral (for comparison with $MeNH_2$). To place the systems on an equal footing, the rate constants have also been calculated on a "per H atom basis" and those for $^{\bullet}O^-$ with anions have been corrected to zero ionic strength using the Debye−Hückel−Brønsted−Davies equation.[19] Finally, to allow for the different BDEs with which the atoms are held, the per H atom rate constants have been plotted in Figure 3, parts a and b, against the exothermicity of the abstraction reaction, $Q_{(Rx)}$ ($=-\Delta H_{(Rx)}$). That approach is based on the Evans−Polanyi relation, which assumes that activation energies fall and rates increase with exothermicity for abstractions involving similar centers.[37] $Q_{(Rx)}$ was calculated from the differences between the BDEs of the abstracted H atoms, D_{C-H}, and those of OH^- and H_2O, D-$_{O-H}$ and D_{HO-H}, respectively. D-$_{O-H}$ and D_{HO-H} were taken as 463 and 499 kJ mol^{-1}, based on data in ref 38. The D_{C-H} values for the sites from which abstraction is assumed to occur are given in the last column of Table 2.

Figure 3a shows the results for $MeNH_2$ and alcohols and Figure 3b those for Gly^- and other anions. For the alcohols specific rates for H-abstractions by $^{\bullet}OH$ from individual α-C or β-C sites were calculated from information in refs 5 and 43. The crosses in Figure 3a are for those specific rate constants. The open points were calculated using the approximation that the total rate was due solely to the site in the molecule with the weakest BDE. In all cases these overlap the crosses, showing that the errors due to the approximation are negligible. The same approximation was used for the alcohol reactions with $^{\bullet}O^-$, where specific rates for α-C or β-C sites are not available. For formate and acetate in Figure 3b, only a single C-site is available in each case.

The rate constants from ref 14, which are used in the comparisons here, have been taken from several different sources and the probable errors are likely about ±50%. The probable error in the logarithms of the rate constants in Figures 3a and b are therefore on the order of ±0.2. The most obvious feature is that the rates of all four types of reaction ($^{\bullet}O^-$/$^{\bullet}OH$ with anionic/neutral compounds) increase linearly with $Q_{(Rx)}$ over the range studied here, and the slopes of the trend lines are quite similar (0.46 ± 0.01 and 0.38 ± 0.01 for the neutrals in Figure 3a and anions in Figure 3b, respectively). Another feature is that at a given value of $Q_{(Rx)}$ in Figure 3a the log(k) value is always higher for $^{\bullet}O^-$ than for $^{\bullet}OH$ by an amount well in excess of the 0.2 error limit. The $MeNH_2$ results fit this pattern in the same way as the values for the alcohols. The most obvious reason for the higher rates with $^{\bullet}O^-$ is the absence of any orientation requirement for this spherically symmetric reactant. By contrast, when $^{\bullet}OH$ is the reactant, the $>C{-}H...{}^{\bullet}OH$ transition states will require a well-defined $H...{}^{\bullet}O{-}H$ angle, and this will cause the steric or entropic factors for the $^{\bullet}OH$ reactions to be lower. In this context, one may note that the gas-phase preexponential factors for H-abstractions from CH_4 and C_2H_6 by $F^{\bullet}$ and $Cl^{\bullet}$ are several times larger than those for $^{\bullet}OH$.[44]

A similar difference in $^{\bullet}O^-$ and $^{\bullet}OH$ reactivity is also apparent for the reactions with the anions in Figure 3b. However, here it is much less pronounced due to the compensating work term arising from the negative charges on the anions and $^{\bullet}O^-$. Calculations based on rudimentary reactant diameters suggest that Coulombic repulsion would reduce the $^{\bullet}O^-$ encounter rate with mono-negative anions by at least a factor of 2 (0.3 on the log scale). More precise estimates will require details of the transition state geometries from ab initio molecular orbital calculations. A comparison of $^{\bullet}\mathrm{O}^-$ and $^{\bullet}\mathrm{OH}$ systems by those methods would also provide information on the entropic effects and barrier heights. Such studies are beyond the scope of this work. However, the plots in Figure 3, parts a and b, demonstrate that the C$-$H abstraction reactions by $^{\bullet}\mathrm{O}^-$ and $^{\bullet}\mathrm{OH}$ fall into a pattern, which is rationalized by reasonable physical arguments. Furthermore, the points for Gly$^-$ reacting with both radicals and for $\mathrm{MeNH_2}$ reacting with $^{\bullet}\mathrm{O}^-$ fall well within the ± 0.2 uncertainty of the lines, consistent with direct C$-$H abstractions. The point for $^{\bullet}\mathrm{OH}$ reacting with $\mathrm{MeNH_2}$ falls outside that limit and was not included in the calculation of the trend line. We will return to this feature later.

Comparison of Observed Total Rate Constants to Diffusion-Controlled Values. The dependences of the partial and per-atom rate constants on $Q_{(\mathrm{Rx})}$ (Figure 3, parts a and b) can only occur if the total rate constants, from which the slower per atom rate constants were obtained, are well below the diffusion-controlled limit, k_{D}. Here it is of interest to determine how close the rate constants for the amino compounds are to this limit. Values of k_{D} can be estimated for Gly$^-$ and $\mathrm{MeNH_2}$ from the following diffusion coefficients, $D_{^{\bullet}\mathrm{OH}} = 2.2 \times 10^{-9}$ m^2 s^{-1},[14] $D_{^{\bullet}\mathrm{O}^-} = D_{\mathrm{F}^-} = 1.5 \times 10^{-9}$ m^2 s^{-1},[45] $D_{\mathrm{Gly}^-} = D_{\mathrm{Ac}^-} = 1.0 \times 10^{-9}$ m^2 s^{-1}, and $D_{\mathrm{methylamine}} = 1.6 \times 10^{-9}$ m^2 s^{-1},[46] and reasonable radii, $R_{^{\bullet}\mathrm{OH}} = R_{^{\bullet}\mathrm{O}^-} = 2 \times 10^{-10}$ m and $R_{\mathrm{Gly}^-} = R_{\mathrm{methylamine}} = 3 \times 10^{-10}$ m. The observed total rate constants for Gly$^-$ and $\mathrm{MeNH_2}$ were already given above. They are repeated in the following sequence with the calculated k_{D} values placed in parentheses beside them, all in units of M^{-1} s^{-1}: (a) for the reaction of Gly$^-$ and $\mathrm{MeNH_2}$ with $^{\bullet}\mathrm{O}^-$, $k = 5.6 \times 10^8$ (5×10^9) and 7.5×10^9 (1.4×10^{10}), respectively; and (b) for the reaction of Gly$^-$ and $\mathrm{MeNH_2}$ with $^{\bullet}\mathrm{OH}$, $k = 2.8 \times 10^9$ (1.3×10^{10}) M^{-1} s^{-1} and 3.6×10^9 (1.3×10^{10}) M^{-1} s^{-1}. The $\mathrm{MeNH_2}$ value for the reaction with $^{\bullet}\mathrm{O}^-$ is a factor of 2 smaller than k_{D}. The other Gly$^-$ and $\mathrm{MeNH_2}$ values are 3$-$10 times lower than k_{D}.

Comparison of N—H and C—H Abstraction. There appears to be relatively little quantitative data on N$-$H abstractions in aqueous solution. Thus, comparisons, similar to that above for the C$-$H abstraction, cannot be made for the amino groups. This section, therefore, focuses on comparisons between the yields of primary $^{\bullet}$NH$-$CHRR$'$ and NH$_2-{}^{\bullet}$CRR$'$ in Table 1. On the basis of the conclusion that ET is negligible for $^{\bullet}\mathrm{O}^-$, one can assume that the relative yields reflect the competition between reactions N($-$H$^{\bullet}$) and C($-$H$^{\bullet}$) in Scheme 1 or, more explicitly, between 27 and 26 for $\mathrm{MeNH_2}$, 18 and 17 for Gly$^-$ and 24 and 23 for Ala$^-$. Thus, on a per atom basis, $k_{\mathrm{N(-H^{\bullet})}}/k_{\mathrm{C(-H^{\bullet})}}$ is found to be 1.6, 0.43, and 0.15 for $\mathrm{MeNH_2}$, Gly$^-$, and Ala$^-$, respectively. Given that the N$-$H bond dissociation enthalpies (BDEs) in this primary amine series should lie in a fairly narrow range, 413 ± 7 kJ mol^{-1} [20b,38] the variation in $k_{\mathrm{N(-H^{\bullet})}}/k_{\mathrm{C(-H^{\bullet})}}$ can be explained by the changes in C$-$H BDEs ($D_{\mathrm{C-H}}$), which are much greater and have been shown above to influence the rates of H abstractions by $^{\bullet}\mathrm{O}^-$ and $^{\bullet}\mathrm{OH}$. $\mathrm{MeNH_2}$ has the largest C$-$H BDE at 393 kJ mol^{-1}. The value for Gly$^-$ is 363[20(b)] and that of Ala$^-$ will be weaker by $\approx$20 kJ mol^{-1}.[47] The observed decrease in $k_{\mathrm{N(-H^{\bullet})}}/k_{\mathrm{C(-H^{\bullet})}}$ is consistent with $k_{\mathrm{C(-H^{\bullet})}}$ increasing with the falling $D_{\mathrm{C-H}}$ in this series.

The authors are unaware of values of $k_{\mathrm{N(-H^{\bullet})}}/k_{\mathrm{C(-H^{\bullet})}}$ for reactions of other O-centered radicals reacting with primary amines. However, Elford and Roberts[48] have studied the reactions of t-BuO$^{\bullet}$ with $\mathrm{Me_2NH}$, and on a per atom, basis their data give $k_{\mathrm{N(-H^{\bullet})}}/k_{\mathrm{C(-H^{\bullet})}} = 11.3$ at 298 K. This larger value for the secondary amine is not unexpected, since the N$-$H BDE is reduced to 380 kJ mol^{-1}.[38] It was also found for this system that the activation energy for $k_{\mathrm{N(-H^{\bullet})}}$ was 4.6 kJ mol^{-1} lower than for $k_{\mathrm{C(-H^{\bullet})}}$,[48] and it has been concluded that, in changing from one abstraction site to another (C$-$H to N$-$H in this case), properties other than parent BDEs may also influence the barrier heights.[49] The fact that the present value of $k_{\mathrm{N(-H^{\bullet})}}/k_{\mathrm{C(-H^{\bullet})}}$ for $\mathrm{MeNH_2}$ is 1.6, although the N$-$H BDE is greater than that of the C$-$H in that compound, implies that this also applies to $^{\bullet}\mathrm{O}^-$.

The yields of $^{\bullet}$NH$-$CHRR$'$ and NH$_2-{}^{\bullet}$CRR$'$ for reaction with $^{\bullet}\mathrm{OH}$ in Table 1 yield $k_{\mathrm{N(-H^{\bullet})}}/k_{\mathrm{C(-H^{\bullet})}}$ ratios of 2.6, 1.0, and 1.1 for $\mathrm{MeNH_2}$, Gly$^-$, and Ala$^-$, respectively. These are much larger than the values of $k_{\mathrm{N(-H^{\bullet})}}/k_{\mathrm{C(-H^{\bullet})}}$ discussed above for $^{\bullet}\mathrm{O}^-$ (1.6, 0.43 and 0.15, respectively). Also, the values for Gly$^-$ and Ala$^-$ do not follow the trend of decreasing with $D_{\mathrm{C-H}}$, and the results cannot be rationalized purely on the basis of the direct H atom abstraction routes. As already stated, any contribution from the indirect ET/C($-$H$^+$) process in Scheme 1 is likely to be small. However, proton transfer is much faster from N$-$H sites, and this would cause the ratio of $^{\bullet}$NH$-$CHRR$'$ and NH$_2-{}^{\bullet}$CRR$'$ yields to be higher as observed. This suggests that a significant fraction of the aminyl radical yields from the $^{\bullet}\mathrm{OH}$ reactions are indeed produced via the ET/N($-$H$^+$) route, which is in competition with the C($-$H$^{\bullet}$) and N($-$H$^{\bullet}$) reactions in Scheme 1.

An interesting point is that the orientational requirements for the ET process, which is the rate-determining step for the ET/N($-$H$^+$) sequence, should be much less restrictive than those for the H-abstraction transition states. Thus, in cases where ET is very efficient, this could cause a reduction in the number of encounters producing H-abstraction by siphoning off encounter pairs before proper $>$C$-$H...$^{\bullet}$OH transition states were formed. The fact that the $^{\bullet}\mathrm{OH}$ C$_\alpha$-H abstraction rate constant for $\mathrm{MeNH_2}$ in Figure 3a is lower than expected on the basis of the data with the alcohols may be a reflection of this.

Conclusions and Summary

The finding that ET is insignificant for $^{\bullet}\mathrm{O}^-$ reactions with the primary amines investigated here is consistent with earlier results from studies with other compounds and with expectations based on its thermodynamic properties. The values of $k_{\mathrm{N(-H^{\bullet})}}/k_{\mathrm{C(-H^{\bullet})}}$ for $^{\bullet}\mathrm{O}^-$ reacting with amines of different C$-$H BDE follow the pattern expected for direct abstraction reactions. By contrast, the values of $k_{\mathrm{N(-H^{\bullet})}}/k_{\mathrm{C(-H^{\bullet})}}$ for $^{\bullet}\mathrm{OH}$ do not. They are much larger and are consistent with aminyl radical formation being enhanced by the indirect ET/N($-$H$^+$) route.

There are relatively few compounds of known C$-$H BDE with which the present rate constants for C$-$H H-abstraction can be compared. However, the per atom rate constants for abstraction from C$-$H sites of $\mathrm{MeNH_2}$ and alcohols by $^{\bullet}\mathrm{O}^-$ and $^{\bullet}\mathrm{OH}$ increase with exothermicity of reaction, and similar correlations were found for $^{\bullet}\mathrm{O}^-$ and $^{\bullet}\mathrm{OH}$ reactions with Gly$^-$, formate, and acetate. $^{\bullet}\mathrm{O}^-$ reactions have a higher steric factor, but this is apparently generally compensated for by more favorable potential energy surfaces associated with the greater exothermicity of $^{\bullet}\mathrm{OH}$ reactions.

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