

The large chemical-shift difference of 42.3 ppm between N1 and N3 of the guanidino group of arginine at  $-52^{\circ}\text{C}$  reflects the average shift difference between the two nitrogens that are cis and trans, respectively, in the mixture of tautomers **4a-c**. In our view, the size of this shift difference, compared to those of other guanidines,<sup>17</sup> almost surely represents a preference for **4b** over **4c** or the reverse. The assignments of the 259.0-ppm and 301.3-ppm peaks to cis or trans nitrogen relative to R must await further study.

Most  $^{15}\text{N}$  NMR spectra of free arginine in aqueous solution, or arginyl residues in proteins, or of intracellular arginine in microorganisms have been taken at or above room temperature and at  $^{15}\text{N}$  resonance frequencies of less than 18 MHz.<sup>24-26</sup> Under such conditions, the resonances of N1 and N3 will be observed as a single peak, because  $k_{\text{ex}} \gg \pi\Delta\nu$ , where  $k_{\text{ex}}$  is the rate of isomerization and  $\Delta\nu$  is the chemical-shift difference in hertz between the nitrogens in the absence of isomerization. However, at 50 MHz ( $^1\text{H}$  resonance frequency of 500 MHz), the N1-N3 peak is considerably broadened and has a  $\nu_{1/2}$  of 30 Hz at  $4^{\circ}\text{C}$  in neutral aqueous solution. Such line broadening resulting from

slow isomerization should be taken into account in  $^{15}\text{N}$  NMR studies of arginine and arginyl residues in enzymes at high magnetic fields.

The guanidinium group of arginine clearly plays an important role in binding anionic substrates and cofactors at the active sites of a number of enzymes.<sup>27</sup> Valuable information on enzyme-substrate complexes and transient intermediates can be obtained by "trapping" them at subzero temperatures in mixed aqueous organic solvents.<sup>28</sup> Applications of NMR for "low-temperature" enzymology are just emerging<sup>29,30</sup> and the nonequivalence of N1 and N3 resonances of arginine at subzero temperatures may be useful in this connection.

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**Registry No.** L-Arginine, 74-79-3.

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## Heats of Formation and Ionization Potentials of Some $\alpha$ -Aminoalkyl Radicals<sup>1</sup>

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**Abstract:** Heats of formation and ionization potentials of  $\alpha$ -aminoalkyl radicals,  $\text{R}_2\text{N}\dot{\text{C}}\text{R}'_2$ , were derived from measurements of the appearance energies for the fragmentations of a series of ethylenediamines. Stabilization energies,  $E_s$ , are high and increase with increasing C- or N-alkylation; the converse applies to ionization potentials, IP. For example, in the case of  $\text{H}_2\text{N}\dot{\text{C}}(\text{Me})_2$ ,  $E_s = 17 \text{ kcal mol}^{-1}$  and IP = 5.4 eV.

The stabilization energies,<sup>3</sup>  $E_s$ , of free radicals, R $\cdot$ , can be increased by appropriate substitution at the radical center (eq 1 and 2). When alkyl groups are adjacent to the unpaired electron

$$\text{BDE}(\text{R}-\text{H}) = \Delta H_f(\text{R}\cdot) + \Delta H_f(\text{H}\cdot) - \Delta H_f(\text{R}-\text{H}) \quad (1)$$

$$E_s = \text{BDE}(\text{CH}_3-\text{H}) - \text{BDE}(\text{R}-\text{H}) \quad (2)$$

the stabilizing effect is relatively small; e.g., the stabilization energies for  $\text{CH}_3\dot{\text{C}}\text{H}_2$ ,  $(\text{CH}_3)_2\dot{\text{C}}\text{H}$ , and  $(\text{CH}_3)_3\dot{\text{C}}$  are 4, 8, and 10  $\text{kcal mol}^{-1}$ , respectively.<sup>4</sup> More pronounced effects are obtained when conjugation with  $\pi$  bonds or electron lone pairs is possible. It is well-known, for example, that allyl,<sup>3,5,6</sup> benzyl,<sup>3,6</sup> and (*E*,*Z*)-pentadienyl<sup>3,7</sup> radicals are highly stabilized with  $E_s = 18, 16,$

and 28  $\text{kcal mol}^{-1}$ , respectively. Lone pairs of electrons on oxygen have a similar effect since for  $\dot{\text{C}}\text{H}_2\text{OH}$ <sup>8</sup> and  $\dot{\text{C}}\text{H}_2\text{OCH}_3$ <sup>9</sup>  $E_s = 8$  and 11  $\text{kcal mol}^{-1}$ , respectively. However, the stabilizing effect due to a nitrogen lone pair has not been thoroughly investigated.

In a preliminary report of this work,<sup>10</sup> we showed that the stabilization energies for  $\alpha$ -aminoalkyl radicals were large and that they showed a rather dramatic dependence on the extent of N-alkylation. We now describe a detailed investigation of this subject.

### Experimental Section

**Apparatus.** The apparatus used in this work has been described in detail elsewhere.<sup>11,12</sup> Briefly, ions were generated in the gas phase by impact of an energy-resolved electron beam from an electrostatic electron monochromator.<sup>11</sup> They were detected by using a quadrupole mass spectrometer coupled with a minicomputer data system.<sup>12</sup> The appearance energy, AE, of a given ion was determined by detecting the threshold for an ion current at the appropriate mass as the energy of the

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Table I

$R_1-R_2$	$\Delta H_f(R_1-R_2)^a$ kcal mol <sup>-1</sup>	AE( $R_1^+$ ), eV	$\Delta H_f^-(R_1^+)^b$ kcal mol <sup>-1</sup>	$\Delta H_f^-(R_2^\cdot)$ , kcal mol <sup>-1</sup>	$\Delta H_f^-(R_2-H)^c$ kcal mol <sup>-1</sup>	BDE- ( $R_2-H$ ), kcal mol <sup>-1</sup>	$E_s(R_2^\cdot)$ , kcal mol <sup>-1</sup>	IP( $R_2^\cdot$ ), eV
Me <sub>2</sub> NCH <sub>2</sub> -CH <sub>2</sub> NMe <sub>2</sub>	-4.7 <sup>c</sup>	8.18 <sup>d</sup>	158	26	-5.7	84	20	5.7
Me <sub>2</sub> NCH <sub>2</sub> -CH <sub>2</sub> NHMe	-3.6	8.32	158	30	-4.4	87	17	5.9
H <sub>2</sub> NCH <sub>2</sub> -CH <sub>2</sub> NH <sub>2</sub>	-4.3	9.56 <sup>e</sup>	177	36	-5.5	94	10	6.1
H <sub>2</sub> N(Me)CH-CH(Me)NH <sub>2</sub>	-20.9	8.86	157	26	-11.4	90	14	5.7
H <sub>2</sub> N(Me) <sub>2</sub> C-C(Me <sub>2</sub> )NH <sub>2</sub>	-36.0	8.41	141	17	-20.0	89	15	5.4

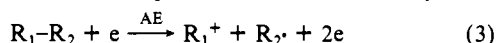
<sup>a</sup> Calculated from group additivity contributions (Benson, S. W.; Cruikshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* 1969, 69, 279. <sup>b</sup> Reference 15. <sup>c</sup> Pedley, J. B.; Rylance, J. "Sussex-N.P.L. Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds"; University of Sussex, 1977. <sup>d</sup> See ref 31. <sup>e</sup> Literature value 9.54 eV by photoionization (Chupka, W. A. *J. Chem. Phys.* 1959, 30, 191).

electron beam was increased by 0.02-eV steps.

**Compounds.** 2,3-Dimethylbutane-2,3-diamine<sup>13</sup> and butane-2,3-diamine<sup>14</sup> were prepared by established procedures. For purification, they were crystallized as their oxalate and hydrochloride salts, respectively. The free amines were then liberated by treatment with base. Other materials were commercially available. All compounds were distilled before use.

### Results and Discussion

The appearance energies, AE, for the fragmentation of a series of ethylenediamines were determined by using mass spectrometry<sup>11,12</sup> (eq 3 and 4). These equations define the thermodynamic



$$AE = \Delta H_f(R_1^+) + \Delta H_f(R_2^\cdot) - \Delta H_f(R_1-R_2) \quad (4)$$

relationship between the appearance energy and the heats of formation of the ion  $R_1^+$ , the radical  $R_2^\cdot$ , and the parent diamine. More precisely, heats of formation derived from eq 4 represent limiting values since appearance energies may be significantly greater than the enthalpic requirement for the fragmentation. This consideration applies equally to the derivation of an unknown  $\Delta H_f(R^+)$  or  $\Delta H_f(R^\cdot)$ . The possibility of error from this source can be substantially reduced by choosing a compound  $R_1-R_2$  for which reaction 3 is the minimum energy dissociation process and by carrying out the measurement of AE with energy-resolved electrons under conditions where the residence time of the parent ion  $R_1-R_2^+$  in the ion source is as long as possible. This generally reduces the "kinetic shift" in the threshold energy to negligible proportions.<sup>12</sup>

The heats of formation of the ions were determined from the appearance energies for the fragmentation of compounds  $R_1-R_2$ , where  $R_1^+$  was the ion used in this work but where the radicals  $R_2^\cdot$  were H,  $\cdot$ CH<sub>3</sub>, and  $\cdot$ CH<sub>2</sub>OH, whose heats of formation were known. The values of  $\Delta H_f(R^+)$  determined in these sets of three experiments<sup>15</sup> were the same within experimental error, implying that eq 4 was valid for these measurements. Moreover, in the present work  $\Delta H_f(R^+)$  is effectively a standard that relates the heats of formation of H,  $\cdot$ CH<sub>3</sub>, and  $\cdot$ CH<sub>2</sub>OH to those of  $\alpha$ -aminoalkyl radicals. As a result, any systematic errors associated with  $\Delta H_f(R^+)$  values will be minimized.

The appearance energies measured in this work are reported in Table I together with values obtained for  $\Delta H_f(R_2^\cdot)$ , BDE( $R_2-H$ ),  $E_s(R_2^\cdot)$ , and IP( $R_2^\cdot$ ) (eq 1, 2, 4, and 5).

$$IP(R_2^\cdot) = \Delta H_f(R_2^+) - \Delta H_f(R_2^\cdot) \quad (5)$$

As shown in the table,  $\alpha$ -aminoalkyl radicals are highly stabilized, and  $E_s$  increases as either C- or N-alkylation is increased. The stabilizing effects of C-alkylation are, of course, preceded in the simple series  $\cdot$ CH<sub>3</sub>, ...,  $\cdot$ C(CH<sub>3</sub>)<sub>3</sub>.<sup>4</sup>

Experiments by Richey and Shull<sup>16</sup> led to the conclusion that the stabilization energy afforded by an NMe<sub>2</sub> group was 19 kcal

mol<sup>-1</sup>. Nevertheless, there was tendency to discount this result on the premise that  $E_s$  should not be significantly affected by N-alkylation. Although recent theoretical results<sup>17</sup> do support such a premise, our results clearly support the earlier experimental observations.<sup>16</sup> Further, we note that EPR data of  $\alpha$ -aminoalkyl radicals suggest that electron delocalization increases with increasing N-alkylation.<sup>18,19</sup> Moreover, it is generally well accepted that N-H bond strengths show a strong dependence on the extent of N-alkylation since BDE(H<sub>2</sub>N-H) = 107 kcal mol<sup>-1</sup>, BDE(MeHN-H) = 100 kcal mol<sup>-1</sup>, and BDE(Me<sub>2</sub>N-H) = 92 kcal mol<sup>-1</sup>.<sup>20</sup> It is, therefore, not too surprising that the related C-H bond strengths are moderated in a similar way.

The thermodynamic properties of  $\alpha$ -aminoalkyl radicals are the key to understanding much of the free-radical chemistry of amines. The very weak C-H bonds in amines make hydrogen abstraction by ketone triplets or alkylperoxy or alkoxy radicals particularly facile. For example, the rate constant for hydrogen abstraction from trimethylamine by *tert*-butoxy radicals is  $1.1 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup><sup>21</sup> and is rivaled only by abstractions at cyclohexadienes<sup>22</sup> or other highly conjugated molecules,<sup>23</sup> which proceed with rate constants in the range  $10^7$ - $10^8$  M<sup>-1</sup> s<sup>-1</sup>. These reactions show a stereoelectronic effect; hydrogen abstraction is most facile when the C-H bond being broken is aligned with the orbital containing the nitrogen lone pair. In addition, rate constants for hydrogen abstraction decrease with decreasing N-alkylation following the trend in C-H bond dissociation energies.<sup>24</sup>

The conjugation in  $\alpha$ -aminoalkyl radicals can be described in terms of the theory of the "three-electron bond".<sup>25</sup> This theory predicts that two of the three electrons in the N-C moiety will be in a bonding orbital while the third will be in an energetically close antibonding orbital. Excitation between these levels should therefore occur at fairly low energies. The UV-visible spectra of  $\alpha$ -aminoalkyl radicals support this concept since they are substantially red shifted with respect to those of alkyl radicals and "tail" into the visible up to ca. 500 nm. For example, in the case of Me<sub>2</sub>NCH<sub>2</sub>,  $\epsilon = 540 \pm 100$  M<sup>-1</sup> cm<sup>-1</sup> at 340 nm,<sup>26</sup> while for Me<sub>2</sub>CH,  $\epsilon = 1000 \pm 50$  M<sup>-1</sup> cm<sup>-1</sup> at 220 nm.<sup>27</sup>

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The ionization potentials for  $\alpha$ -aminoalkyl radicals are the lowest observed for any organic or organometallic species.<sup>28</sup> Moreover, they decrease with increasing C- or N-alkylation. They are substantially lower than ionization potentials for simple alkyl radicals, which fall on the range 7–10 eV,<sup>28</sup> and are close to those for lithium (5.39 eV) and sodium (5.14 eV). The description of  $\alpha$ -aminoalkyl radicals as "organic metals"<sup>29</sup> seems to be entirely appropriate.

$\alpha$ -Aminoalkyl radicals are powerful reducing agents by virtue of their low ionization potentials. This has prompted the use of amines as sacrificial donors in photochemical reductions<sup>30</sup> because

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the  $\alpha$ -aminoalkyl radicals thus formed generally carry out a second chemical reduction, effectively doubling the overall quantum yield.

To summarize,  $\alpha$ -aminoalkyl radicals have remarkably high stabilization energies and low ionization potentials. Stabilization energies increase and ionization potentials decrease with increasing C- or N-alkylation. These thermodynamic properties underlie many of the observed chemical properties of  $\alpha$ -aminoalkyl radicals and their parent amines.

**Registry No.** Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>, 110-18-9; Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NHMe, 142-25-6; H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, 107-15-3; H<sub>2</sub>N(Me)CHCH(Me)NH<sub>2</sub>, 563-86-0; H<sub>2</sub>N(Me)<sub>2</sub>CC(Me)<sub>2</sub>NH<sub>2</sub>, 20485-44-3; Me<sub>2</sub>NCH<sub>2</sub><sup>+</sup>, 30208-47-0; MeNHCH<sub>2</sub><sup>+</sup>, 31277-24-4; H<sub>2</sub>NCH<sub>2</sub><sup>+</sup>, 10507-29-6; H<sub>2</sub>N(Me)CH<sub>2</sub><sup>+</sup>, 30208-36-7; H<sub>2</sub>N(Me)<sub>2</sub>C<sup>+</sup>, 26374-12-9.

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## Mechanism of the Ozonolysis of Propene in the Liquid Phase

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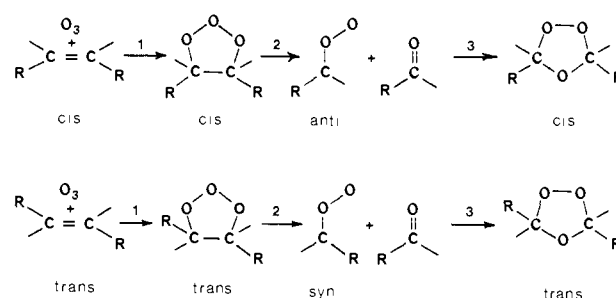
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**Abstract:** Propylene was ozonized in isobutane, chlorodifluoromethane, and methyl chloride solvents. Propylene ozonide, ethylene ozonide, and 2-butene ozonide (cis and trans isomers) were obtained in ratios of about 82:16:2. The amount of butene ozonide increased while that of ethylene ozonide usually decreased for reactions in the presence of added acetaldehyde. The cis-trans stereochemistry of the butene cross ozonide from propylene was studied at various conditions. Usually the cis isomer was preferentially formed, but addition of acetaldehyde could alter this. The cis/trans-butene ozonide ratio was 67/33 when formed from cis- or trans-2-butene in CHCl<sub>3</sub> and 50/50 as a cross ozonide from trans-2-pentene. The kinetic secondary isotope effects upon ozonolysis of propene-2-d<sub>1</sub> ( $k_H/k_D = 0.88$  (6)) and propene-1-d<sub>1</sub> (0.88 (8)) were evaluated. These results are discussed with reference to the Criegee mechanism of ozonolysis.

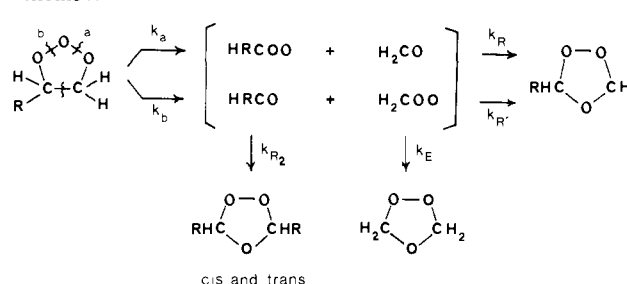
It has been documented that a cis(trans)-alkene upon ozonolysis usually yields more cis (trans) final ozonide.<sup>2-4</sup> One rationale for this, the three-step concerted Criegee mechanism, is outlined in Scheme I and applies to the predominant process for the cis- or trans-alkene.<sup>5</sup> The most comprehensive presentations of this model were first forwarded qualitatively and inferentially by reaction chemists.<sup>8,9</sup>

One difficulty encountered by this proposal arises with small alkenes such as 2-butene and 2-pentene. For these cases, more trans ozonide has been observed irrespective of the alkene configuration.<sup>8-11</sup> In a series of papers,<sup>12</sup> Cremer has suggested a

Scheme I



Scheme II



solution to this puzzle. Guided by energy calculations, he has argued that step 2 in Scheme I is endothermic or nearly thermally

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