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Semiempirical prediction of the thermochemistry of intermediates involved in the cyclic mechanism of hindered amine stabilizers

Jeffrey M. Cogen

Polyolefins Division, Union Carbide Corporation, CN 450, Somerset, New Jersey 08875-0450, USA

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The suitability of the AM1 computational method for predicting the thermochemistry of amine derivatives related to the functioning of hindered amine light stabilizers (HALS) was established by comparing computed data with representative published experimental data for HALS-related intermediates. Thus, AM1 accurately predicts the relative energies of 2,2,6,6-tetramethyl-4-oxopiperidine, 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl and 1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidine. The AM1 method was then utilized to estimate key bond dissociation energies for which experimental values do not exist. For the 2,2,6,6-tetramethyl-4-oxopiperidine series the following bond strengths are predicted: $\text{N—O}^{\cdot} = 366$ kJ/mol; $\text{N—OH} = 234$ kJ/mol; $\text{NO—H} = 296$ kJ/mol; $\text{N—OCH}_3 = 176$ kJ/mol; $\text{NO—CH}_3 = 185$ kJ/mol; $\text{NOCH}_2\text{—H} = 359$ kJ/mol; $\text{N—OC}_2\text{H}_5 = 164$ kJ/mol; $\text{NO—C}_2\text{H}_5 = 172$ kJ/mol; $\text{NOCH}_2\text{—HCH}_3 = 344$ kJ/mol; $\text{N—OCH(CH}_3)_2 = 143$ kJ/mol; $\text{NO—CH(CH}_3)_2 = 154$ kJ/mol; $\text{NOC—H(CH}_3)_2 = 333$ kJ/mol. The data should be of general value for the thermodynamic evaluation of proposed HALS mechanisms.

INTRODUCTION

The rapid growth in the use of hindered amine light stabilizers (HALS) in a wide variety of applictions has been accompanied by an improved understanding of the mechanisms by which they function.[1–3] Nevertheless, there is not yet agreement on which are the dominant mechanisms under real end-use conditions. Recent attention has focussed on the mechanism of regeneration of nitroxyl from the *N*-alkoxyamine. Though it has been widely believed that an alkylperoxy radical and an *N*-alkoxyamine react to regenerate the nitroxyl radical and a dialkylperoxide (Denisov mechanism),[3] recent model studies by Klemchuk and coworkers[1,2] have led to the proposal of an alternative mechanism, in which the nitroxyl is regenerated from the *N*-alkoxyamine with concomitant formation of a carbonyl compound and an alcohol and consumption of an alkylperoxy radical. While it is possible that the operative mechanism(s) may depend to some extent on the specific conditions encountered, it is generally agreed that key intermediates include nitroxyl radicals, *N*-alkoxyamines and *N*-hydroxylamines.

In the study of organic reaction mechanisms it is essential to assess the thermodynamics involved in any reaction under evaluation.[4] In the case of many of the reactions proposed to be involved in the functioning of HALS this has not been possible since the thermodynamic data required for such evaluations are not available. The value of such information was illustrated in a recent study[5] which modeled the Klemchuk and Denisov mechanisms using the AM1 computational method, and helped to illustrate the

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potential value of semiempirical quantum-chemical techniques in studying HALS mechanisms.

The goal of this study is twofold. First, since parameterization of AM1 did not explicitly include *N*-oxide derivatives such as nitroxyl radicals, *N*-alkoxyamines and *N*-hydroxylamines, it is desired to establish the accuracy for such compounds by comparing computed data with the limited available experimental data for HALS-related intermediates. The second goal of this study is to provide reliable estimates of important, but unmeasured, thermochemical properties of intermediates related to the functioning of HALS, using the AM1 computational method.[6–10]

METHODS

Calculations were run using the AM1 program through the PC version of HyperChem, available from Autodesk. All reported heat of formation data are believed to represent global minima. All calculations on radicals were run using the 'half electron' method.[11,12] A convergence limit of 0·01 kcal/mol (0·04 kJ/mol) was used in all calculations, with a termination condition RMS gradient of 0·100 kcal/Å mol (0·420 kJ/Å mol). All reported heat of formation and heat of reaction data correspond to the gas-phase at 25°C (298 K). From heat of formation values, the heat of reaction is obtained using the following equation:

$$\Delta H_{\mathrm{rxn}} = \Sigma\ (\Delta H_{\mathrm{f}}^{0}\ \text{products}) - \Sigma\ (\Delta H_{\mathrm{f}}^{0}\ \text{reactants})$$

RESULTS AND DISCUSSION

Experimental gas-phase heat of formation data for 2,2,6,6-tetramethyl-4-oxopiperidine (TMOP), 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl, and 1-hydroxy-2,2,6,6-tegramethyl-4-oxopiperidine have been reported.[4] At the start of the present study it was, therefore, of interest to compare the experimental data with those calculated using AM1 to establish the ability of AM1 to handle the relative energies of these types of molecules. The results are shown in Fig. 1. In keeping with the tendency of AM1 to calculate highly branched molecules as slightly too unstable,[6–10] the AM1 values are all higher than the experimental values. However, as is often the case with these types of error, a closer look reveals that the error is systematic. The average absolute error for the three is +44 ± 2 kJ/mol. Since the error in this series is nearly constant, it will cancel in any equations that have a derivative related to TMOP on each side of the equation. (Alternatively, a −44 kJ/mol correction can be applied to the intermediates in question to obtain estimates of the absolute heats of formation.) This concept is demonstrated by comparing enthalpies for reaction of TMOP with the hydroperoxy radical and reaction of 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl with a hydrogen atom predicted using AM1 to those calculated using experimental heats of formation (Fig. 1). In both cases, AM1 correctly predicts the heats of reaction to within the uncertainty in the measurement of the experimental values.

Without additional experimental values it is not possible to make a more reliable estimate of the error involved in the present AM1 predictions. However, it can be pointed out that in a test series calculated by Dewar *et al.*[8] using the AM1 method, the mean absolute error for 14 neutral radical heats of formation was 33·5 kJ/mol. For the two aminyl radicals tested the mean error was only 9·8 kJ/mol. In most cases the radicals were predicted to be slightly too stable. The mean absolute error for the heats of formation of the 138 closed shell molecules originally tested was 23·2 kJ/mol. For molecules

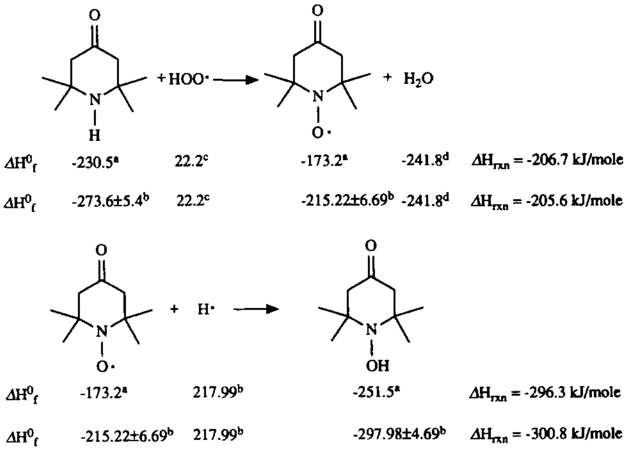

Fig. 1. Comparison of AM1 (first line of each series) and experimental (second line of each series) heats of formation (kJ/mol) and heats of reaction involving three TMOP derivatives. Although the absolute values of heat of formation are all high with AM1, the relative energies and absolute heats of reaction are accurately reproduced. ([a] AM1 (this work); [b] Ref. 4; [c] Ref. 15; [d] Ref.16.)

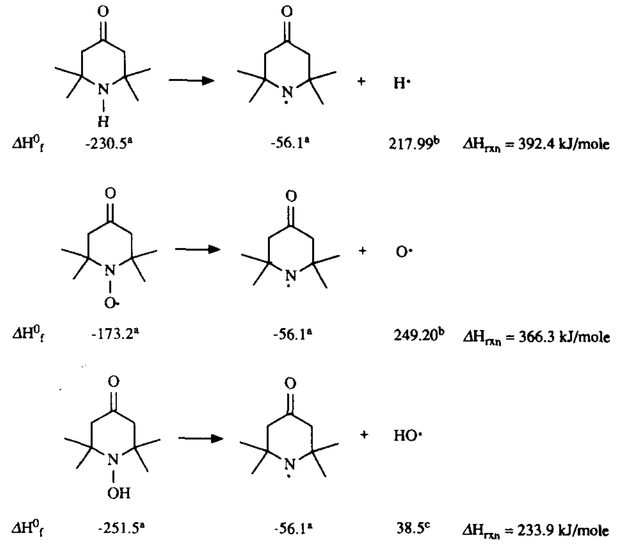

Fig. 2. Relative heats of formation (kJ/mol) and absolute heats of reaction (bond dissociation energies) involving some key TMOP derivatives predicted using AM1. ([a]AM1 (this work); [b] Ref. 4; [c] Ref. 15.)

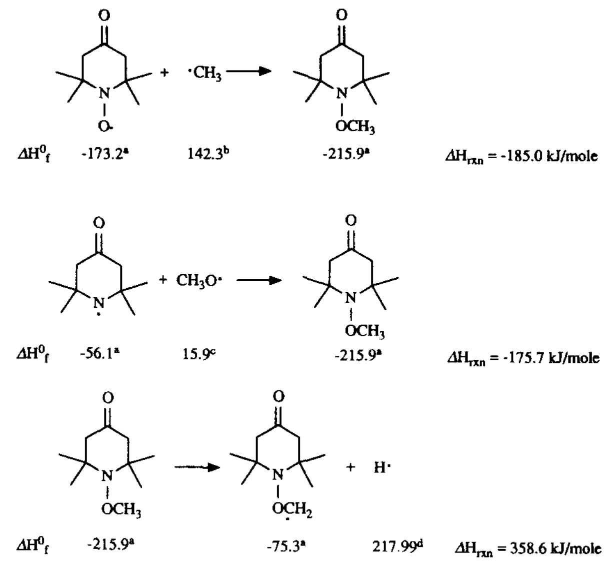

Fig. 3. Relative heats of formation (kJ/mol) and absolute heats of reaction (bond dissociation energies) involving the *N*-methoxyamine derived from TMOP predicted using AM1. ([a] AM1 (this work); [b] Ref. 17; [c] Refs 18 and 19; [d] Ref. 4.)

containing nitrogen and/or oxygen the average error was 24·6 kJ/mol. It is important to note that the above test cases included many different bonding situations, with emphasis on those which had problems in the predecessor MINDO/3 and MNDO programs. Therefore, it is estimated that the mean error in the bond energies predicted in the present study should be well below 42 kJ/mol.

Having established that the method correctly handles the relative energies of the amine and representative *N*-oxides, we turned to TMOP derivatives for which experimental thermochemical data are not yet available. The results so obtained will permit generalizations to be made about bond strengths in related systems. AM1 heats of formation and heats of reaction for some interesting intermediates and reactions are tabulated in Figs 2 to 5.

Summarizing the results shown in Figs 1 to 5, the following ranges are predicted for the various bond strengths of interest in the study of HALS mechanisms: N—O$^{\cdot}$ = 366 kJ/mol; N—OH = 234 kJ/mol; NO—H = 296 kJ/mol; N—OCH_3 = 176 kJ/mol; NO—CH_3 = 185 kJ/mol; $NOCH_2$—H = 359 kJ/mol. The bonds in the ethoxy series are N—OC_2H_5 = 164 kJ/mol; NO—C_2H_5 = 172 kJ/mol; $NOCH_2$—HCH_3 = 344 kJ/mol. The bonds in the isopropoxy analogues, N—$OCH(CH_3)_2$, NO—$CH(CH_3)_2$ and NOC—$H(CH_3)_2$ are calculated to be 143, 154 and 333 kJ/mol, respectively. These data are summarized in Table 1. These low values predicted by AM1 for the N—OR and NO—C bond dissociation energies are consistent with the 88 to 134 kJ/mol activation energies measured for the thermal decomposition of various highly substituted *N*-alkoxytetramethylpiperidines.[13] The relatively low bond strengths of the N—O and C—O bonds predicted for the alkoxyamine intermediates, comparable to the O—O bond strength in

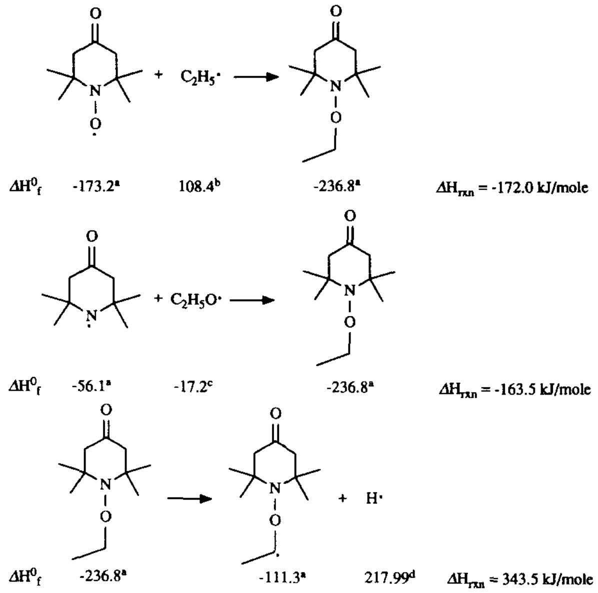

Fig. 4. Relative heats of formation (kJ/mol) and absolute heats of reaction (bond dissociation energies) involving the *n*-ethoxyamine derived from TMOP predicted using AM1. ([a] AM1 (this work); [b] Ref. 17; [c] Ref. 18; [d] Ref. 4.)

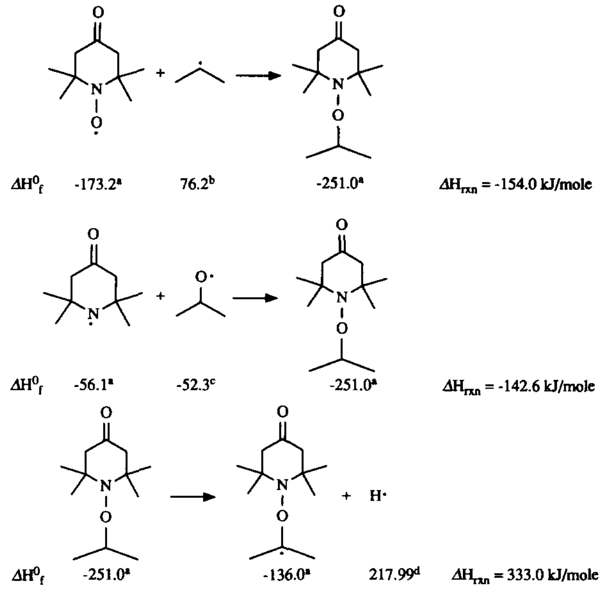

Fig. 5. Relative heats of formation (kJ mol) and absolute heats of reaction (bond dissociation energies) involving the *N*-isopropoxyamine derived from TMOP predicted using AM1. ([a] AM1 (this work); [b] Ref. 17; [c] Ref. 18; [d] Ref. 4.)

peroxides, may explain the observation[14] that HALS often lose their efficacy at elevated temperatures.

The bond strength of the C—H bond adjacent to the oxygen in *N*-alkoxyamines is predicted to be between 333 and 359 kJ/mol in these cases. Such low values, comparable with those of the O—H hydrogens in hindered phenols (typically *c.* 360 kJ/mol), indicate that this hydrogen should be readily abstracted by many types of radicals, a finding which opens the possibility for some interesting mechanisms. Figure 6 indicates one such possibility and demonstrates the application of the results obtained in this study. In the novel process, a radical abstracts the weak hydrogen on the carbon atom adjacent to the oxygen of the *N*-alkoxyamine. The intermediate radical can then undergo cleavage, driven by formation of the strong carbonyl bond and the aminyl radical. The aminyl radical can then enter back into the catalytic cycle directly after reaction with oxygen or after abstracting a hydrogen to form the parent amine.

Table 1. Bond dissociation energies (kJ/mol) predicted for TMOP derivatives using AM1. Reported values are for the bonds indicated by the dashes

	TMOP
$R_2N—O^{\cdot}$	366
$R_2N - OH$	234
$R_2NO—H$	296
$R_2N—OCH_3$	176
$R_2NO—CH_3$	185
$R_2NOCH_2—H$	359
$R_2N - OC_2H_5$	164
$R_2NO—C_2H_5$	172
$R_2NOCH_2—HCH_3$	344
$R_2N—OCH(CH_3)_2$	143
$R_2NO—CH(CH_3)_2$	154
$R_2NOC—H(CH_3)_2$	333

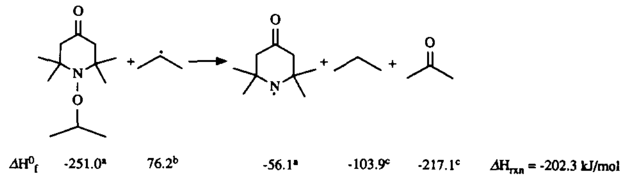

Fig. 6. Demonstration of the application of the AM1 results to evaluate the thermodynamics of a novel hypothetical HALS regenerative mechanism. A similar favorable mechanism can be drawn involving an alkylperoxy radical instead of an alkyl radical. Heats of formation are in kJ/mol. ([a] AM1 (this work); [b] Ref. 17; [c] Ref. 4.)

CONCLUSION

The AM1 method was shown to predict accurately the relative energies of representative hindered amine and *N*-oxide derivatives for which experimental values are available, and then used to predict the thermochemistry of HALS intermediates for which experimental values are not available. In addition to providing data that should be of general use in evaluating the feasibility of HALS mechanisms in the future, the results establish that the AM1 method is suitable for broader use in the study of HALS mechanisms. The utility of the thermochemical estimates was then demonstrated by evaluation of the thermodynamics of a novel hypothetical mechanism.

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