

Applications of the PM3 semi-empirical method to the study of triethylenediamine

J. Mancuso and R.J. McEachern*

AECL, Whiteshell Laboratories, Pinawa, Manitoba, Canada

Charcoal filters impregnated with triethylenediamine (TEDA) are known to be efficient for the collection of volatile methyl iodide, which may be released under a hypothetical loss-of-coolant accident in a nuclear generating station. The structure and thermodynamic stability of the products of the TEDA-methyl iodide reaction have thus been studied using semi-empirical techniques. The reaction of TEDA with two molecules of methyl iodide leads to a quaternization reaction at each of the nitrogens. Moreover, it is shown that substitution of the hydrogens on TEDA with electron-donating groups can lead to enhanced stability of the quaternary ammonium reaction products. The semi-empirical method PM3 (Parametric Method 3) was used as the basis for all calculations. Molecular systems and simulations were constructed using HyperChem 4.5 for Silicon Graphics workstations. Enthalpy determination and geometry optimization were some of the calculations performed on a system. © 1997 by Elsevier Science Inc.

Keywords: semi-empirical, PM3, molecular modeling, triethylenediamine, TEDA, iodomethane, enthalpy

INTRODUCTION

Triethylenediamine (TEDA) is widely used as an impregnant on charcoal filters for the removal of noxious gases such as SO₂ and HCN from air streams^{1,2} and also for removal of airborne radioiodine from nuclear reactors in the event of an accident^{3,4}. The TEDA on the surface of charcoal chemisorbs iodine-containing organic compounds such as methyl iodide by way of well-known quaternization reactions (Figure 1)⁵⁻⁷.

Filters impregnated with TEDA show high efficiency for methyl iodide removal when they are new, but their effective-

ness is slowly degraded by adsorption of moisture and other contaminants⁸⁻¹¹. Charcoal filters impregnated with several different TEDA analogs (including quaternary salts and alkyl-substituted compounds) have been investigated in an effort to minimize deterioration of filter performance over time^{12,13}. In the present study, we report results of semi-empirical calculations modeling the reaction between TEDA and various organic iodine compounds to illustrate the utility of such a computational method and to identify TEDA analogs that may prove useful in charcoal filters.

CALCULATIONS

All calculations in this study were performed with HyperChem, version 4.5®, for the Silicon Graphics® (Hypercube Inc., Waterloo, Ontario, Canada) Indigo workstation. The semi-empirical PM3^{14,15} method, which is based on the NDDO¹⁴ approximation, was used in the present study because it provides a reasonably accurate, rapid estimation of heats of formation. We are thus able to compare the relative energetics for the reaction between TEDA (or its analogs) with a series of organic iodine compounds.

The TEDA analogs were created by adding one substituent to each carbon on one of the carbon bridges. The substituents were placed in a *trans* configuration relative to each other for stereochemical equivalency and minimization of any steric effects (Figure 2). Geometry optimizations were then performed, and the heat of formation was obtained for the TEDA analogs, as well as for the mono- and bisquaternary derivatives obtained by reaction of these compounds with iodomethane.

RESULTS

The optimized geometric configurations of TEDA and its analogs were calculated by standard methods with the HyperChem code. The connectivity of the atoms within each molecule was specified and then the model builder was invoked to provide reasonable starting geometries for the optimization. No significant difficulties were encountered with geometry optimization of TEDA or its analogs. Calculated

Color Plates for this article are on page 101.

*Address correspondence to: R.J. McEachern, AECL, Whiteshell Laboratories, Pinawa, Manitoba, ROE 1L0 Canada.

Paper submitted to the Electronic Conference of the Molecular Graphics and Modelling Society, October 1996.

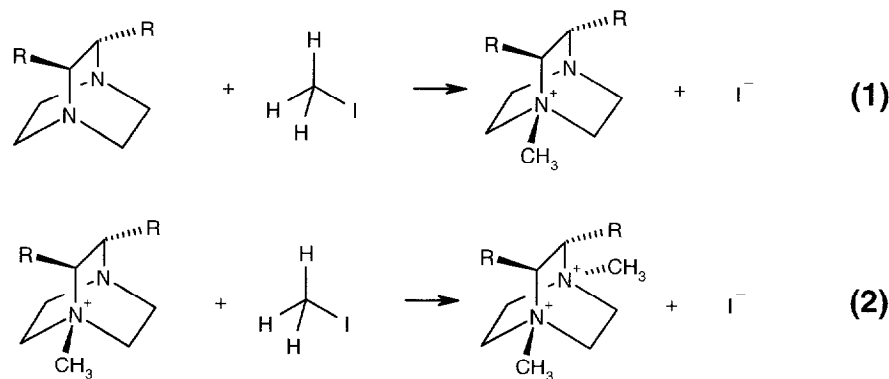


Figure 1. Quaternization reactions of TEDA and iodomethane.

bond lengths and angles were all within the expected ranges, e.g., for TEDA, C–C = 0.154 nm, C–H = 0.111 nm, and C–N = 0.150 nm. The optimized structure of TEDA is illustrated in Color Plate 1. The quaternary salts (Reactions 1 and 2; see Figure 1) did not display any significant Coulombic interaction between the ion pairs, but this is not surprising because our calculations were performed with a semi-empirical method; such procedures often have difficulty modeling the interaction between two gas-phase molecules or ions¹⁴.

Enthalpy of reaction for TEDA and its analogs

Reaction enthalpies for reactions (1) and (2) were calculated for TEDA and a number of its analogs. For each molecule studied, the standard heat of formation was generated in the course of geometry optimization by the PM3 method with HyperChem. The standard heats of formation for TEDA and each of the analogs studied are presented in Tables 1 and 2, along with the calculated heats of reaction.

Standard reaction enthalpies shown in Tables 1 and 2 were calculated by subtracting the sum of the formation enthalpies of the reactants from those of the products. The enthalpies of reactions, displayed in Tables 1 and 2, are positive because the PM3 method does not accurately predict the stability of gas-phase ion pairs, such as the products of Reactions (1) and (2). Thus the reported product enthalpies are for isolated ions. In reality, the stability of the reaction products will be enhanced by crystallization of the quaternary products as ionic salts or by

adsorption of the products on the surface of the charcoal. In the present study, we are examining the effect of varying the substituents for a series of TEDA analogs; thus we are satisfied with calculated reaction enthalpies *relative* to the unsubstituted TEDA molecule. Thus the normalized reaction enthalpies (ΔH_N°) were calculated for each TEDA analog by subtracting the reaction enthalpy for the unsubstituted TEDA molecule. Our analysis includes the implicit assumption that reaction product stability associated with salt formation and/or surface adsorption is the same for TEDA as for the various analogs. Clearly such an assumption is valid only to a first approximation. However, the calculations reported herein are only a preliminary study of the performance of TEDA analogs; the actual performance of such filters would need to be experimentally verified to take into account reaction enthalpy, degree of impregnation of the TEDA analog on the charcoal surface, and the behavior of the reaction product species.

Chemical intuition suggests that substitution of some of the hydrogens on the carbon bridges of TEDA with electron-donating groups should increase the electron density around the nitrogen atoms. This could improve the ability of the TEDA molecule to act as a nucleophile in an S_N2 -type reaction. The extent to which such substituted TEDA molecules react with compounds such as iodomethane will thus vary according to the nature of the substituent. It is interesting to determine the extent to which a fairly modest computational method such as PM3 can model the substituent effects in TEDA.

Table 1 includes substituent field (\mathcal{F}) and resonance (\mathcal{R}) parameters, which measure the electron acceptance or donation capability of a functional group relative to hydrogen¹⁶. Positive parameter values indicate electron-withdrawing capability of the substituent, whereas negative values indicate electron-donating capability. For example, alkyl groups are primarily electron donating according to their field and resonance effects, whereas halogens are electron withdrawing by field effects and weakly donating by resonance.

Quantitative comparison of the calculated values of ΔH_N° with experimental data is not possible because these data do not appear to have been reported yet. However, the trend in reaction enthalpies given in Tables 1 and 2 seems reasonable. The overall trend indicates that the field effect of a substituent has a greater impact on ΔH_N° than does the resonance effect. Substituents with negative field effects reduce the reaction enthalpy regardless of their resonance effects (e.g., alkyls, trimethylsilane, 2-siliconeopentyl). The two substituents

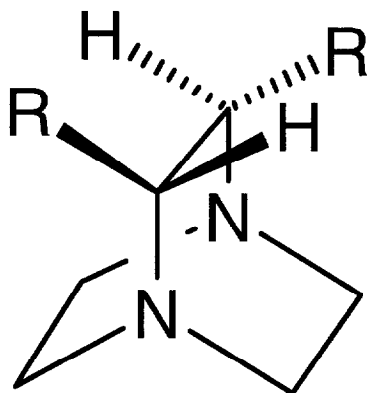


Figure 2. Structure of TEDA analogs.

Table 1. Enthalpy of reaction for the formation of the monoquaternary salt of TEDA and its analogs

Substituent (R) ^a	Field parameter (\mathcal{F}) ^b	Resonance parameter (\mathcal{R}) ^b	Heat of formation (kcal/mol)		Heat of reaction (kcal/mol) ^c	
					ΔH° [Reaction (1)]	ΔH_N° [Reaction (1)]
			R-TEDA	Methyl-R-TEDA		
-Si(CH ₃) ₃	-0.10	0.16	-81.6	64.2	71.8	-14.1
-CH ₂ Si(CH ₃) ₃	-0.19	-0.32	-88.5	60.3	74.8	-11.1
-C ₆ H ₅	0.25	-0.37	62.8	217.3	80.5	-5.4
-OCH(CH ₃) ₂	0.90	-2.88	-90.6	64.1	80.7	-5.2
-N(CH ₃) ₂	0.69	-3.81	9.5	164.7	81.2	-4.7
-CH ₂ CH ₃	-0.02	-0.44	-18.1	138.9	82.9	-3.0
-OCH ₃	0.54	-1.68	-69.6	87.7	83.2	-2.7
-CH ₃	-0.01	-0.41	-8.5	149.1	83.6	-2.3
-NH ₂	0.38	-2.52	14.6	172.5	83.9	-2.0
-tBu	-0.11	-0.29	-30.6	127.8	84.3	-1.6
-OH	0.46	-1.89	-80.6	78.2	84.8	-1.1
-H	0.00	0.00	2.5	162.4	85.9	0.0
-SCH ₃	0.68	-1.30	16.6	177.1	86.5	0.6
-SH	0.52	-0.26	27.0	191.8	90.7	4.8
-Cl	0.72	-0.24	-7.6	160.0	93.6	7.7
-I	0.65	-0.12	53.3	222.7	95.4	9.5
-F	0.74	-0.60	-85.5	85.3	96.7	10.8
-CF ₃	0.64	0.76	-307.1	-126.6	106.6	20.7

^a Substituents are sorted according to increasing reaction enthalpy.

^b Negative values indicate degree of electron donation. Positive values indicate degree of electron acceptance. Values are relative to hydrogen ($\mathcal{F} = 0$, $\mathcal{R} = 0$) and NO₂ ($\mathcal{F} = 1$, $\mathcal{R} = 1$).

^c Heats of formation of iodine = -64.625 kcal/mol, and iodomethane = 9.394 kcal/mol.

containing silicon are those that reduce the reaction enthalpy the most. This is due to the lower electronegativity of silicon (with respect to carbon),¹⁷ which enables electrons to be efficiently shifted from the methyl groups to the nitrogens.

A substituent with a positive field effect can reduce the reaction enthalpy if it has a relatively large negative resonance effect (e.g., amino, dimethylamino, hydroxy, and alkoxy groups). Halogens have positive field effects with small negative resonance effects and will increase the reaction enthalpy.

A linear regression was performed to determine an empirical relationship between reaction enthalpy, ΔH_N° and the field (\mathcal{F}) and resonance (\mathcal{R}) components of the substituent effects on chemical reactivity, as defined by Swain et al.¹⁶ The results of the regression showed that the normalized reaction enthalpies can be described by the expressions:

$$\Delta H_N^\circ(1) = 19.47\mathcal{F} + 4.76\mathcal{R} - 2.95 \quad (3)$$

$$\Delta H_N^\circ(2) = 19.31\mathcal{F} + 4.80\mathcal{R} - 8.20 \quad (4)$$

The linear regression analysis used to produce Eqs. (3) and (4) displayed good residuals for both \mathcal{F} and \mathcal{R} . Moreover, the *F* ratio (i.e., of the mean squares of the regression to that of the residual) test indicates that both field and resonance components contribute significantly (>95% confidence level) to the stability of the quaternary product. Our results thus confirm that both field and resonance components of the substituent effect can have a significant impact on the reaction enthalpy for the quaternization reactions [Reactions (1) and (2)] for TEDA analogs.

To illustrate the effect of the various substituents on the enthalpy change for Reaction (1), a plot was made of the PM3-calculated values of ΔH_N° [Reaction (1)] versus the values obtained with Eq. (3). The resulting plot is shown in Figure 3, and the analogous plot for Eq. (4) data is shown in Figure 4. The scatter in Figures 3 and 4 illustrates deviations between reaction enthalpies calculated by the two different methods; i.e., it is a measure of the "goodness of fit" for the linear expressions (3) and (4). The mean deviation between Reaction

Table 2. Enthalpy of reaction for the formation of the bisquaternary salt of TEDA and its analogs

Substituent (R) ^a	Field parameter (\mathcal{F}) ^b	Resonance parameter (\mathcal{R}) ^b	Heat of formation (kcal/mol)		Heat of reaction (kcal/mol) ^c	
					ΔH° [Reaction (2)]	ΔH_N° [Reaction (2)]
			Methyl-R-TEDA	Dimethyl-R-TEDA		
-Si(CH ₃) ₃	-0.10	0.16	64.2	290.4	152.1	-25.9
-CH ₂ Si(CH ₃) ₃	-0.19	-0.32	60.3	292.2	157.9	-20.1
-OCH(CH ₃) ₂	0.90	-2.88	64.1	302.2	164.0	-14.0
-C ₆ H ₅	0.25	-0.37	217.3	456.2	164.9	-13.1
-N(CH ₃) ₂	0.69	-3.81	164.7	404.7	166.0	-12.0
-NH ₂	0.38	-2.52	172.5	417.6	171.0	-7.0
-tBu	-0.11	-0.29	127.8	373.0	171.1	-6.9
-OCH ₃	0.54	-1.68	87.7	333.1	171.5	-6.6
-CH ₂ CH ₃	-0.02	-0.44	138.9	384.7	171.8	-6.3
-SCH ₃	0.68	-1.30	177.1	423.3	172.2	-5.8
-CH ₃	-0.01	-0.41	149.1	397.5	174.3	-3.7
-OH	0.46	-1.89	78.2	328.9	176.7	-1.3
-SH	0.52	-0.26	191.8	443.8	177.9	-0.1
-H	0.00	0.00	162.4	414.5	178.0	0.0
-I	0.65	-0.12	222.7	475.0	178.3	0.3
-Cl	0.72	-0.24	160.0	415.0	181.0	3.0
-F	0.74	-0.60	85.3	347.0	187.7	9.6
-CF ₃	0.64	0.76	-126.6	140.1	192.6	14.6

^a Substituents are sorted according to increasing reaction enthalpy.

^b Negative values indicate degree of electron donation. Positive values indicate degree of electron acceptance. Values are relative to hydrogen ($\mathcal{F} = 0$, $\mathcal{R} = 0$) and NO₂ ($\mathcal{F} = 1$, $\mathcal{R} = 1$).

^c Heats of formation of iodine = -64.625 kcal/mol, and iodomethane = 9.394 kcal/mol.

(1) enthalpies calculated by the PM3 method and those obtained with Eq. (3) was 3.7 kcal/mol (0.239 kcal/mol = 1 kJ/mol), whereas the analogous deviation for Reaction (2) was 6.0 kcal/mol. (see Tables 3 and 4). In comparison, the average (unsigned) deviation between experimental and calculated heats of formation reported by Stewart was 8.6 kcal/mol¹⁴.

The quaternary N-CH₃ bond length is plotted in Figure 5 as a function of electronegativity of the substituent^{18,19}. The data in Figure 5 illustrate that a decrease in substituent electronegativity will decrease the length of the bond between the quaternary nitrogen and the methyl group. This is consistent with our data, in that a weakly electronegative substituent will not greatly withdraw electron density from around the nitrogen atom. Therefore, the formation of another TEDA nitrogen-alkyl bond (in a quaternization reaction) would be favored.

Reaction of TEDA with iodoalkanes

Most of the results presented herein have focused on the reaction of TEDA (and its analogs) with iodomethane. Reac-

tions (1) and (2) have been the primary focus of the present study because iodomethane is generally used as the organic iodide compound in reactor containment-gas source-term analysis²⁰. However, there are, of course, other organic iodine compounds that would be found in containment, and the reactivity of such compounds (relative to that of iodomethane) toward TEDA is of interest. Calculations such as those presented herein are an ideal way to easily obtain an estimate of the reactivity of a range of iodine compounds toward TEDA-impregnated charcoal filters. We have thus calculated the reaction enthalpy for the monoquaternization reaction between TEDA and various iodine-containing organic compounds. The results are presented in Table 5, as are the efficiencies of TEDA-impregnated charcoal filters at removing these same organic iodine compounds from an air stream²⁰. The calculated reaction enthalpies are compared with the charcoal filter removal efficiency in Figure 6. Note that the datum for diiodomethane has been treated as an outlier in Figure 6. The observed high removal efficiency for diiodomethane is perhaps

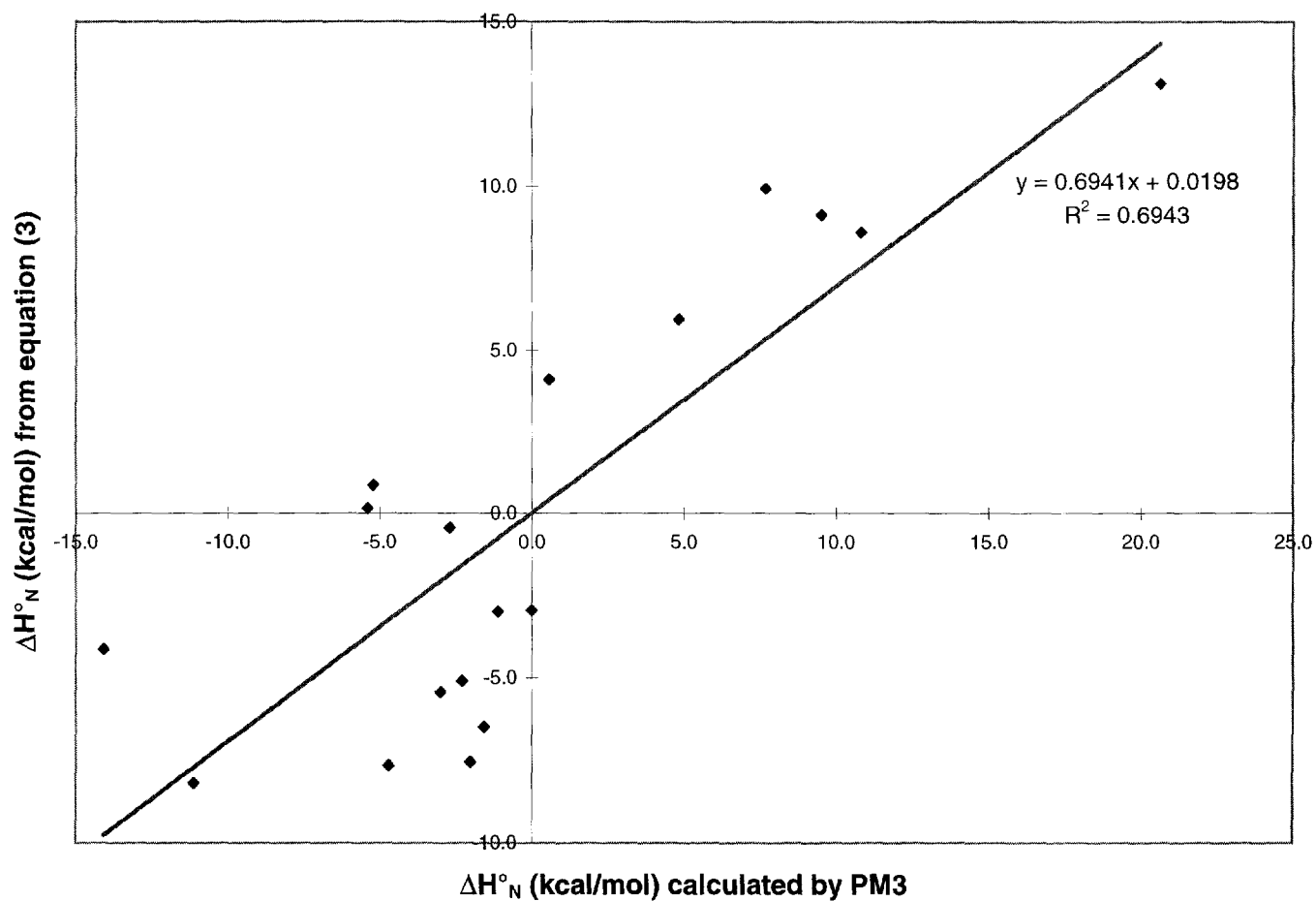


Figure 3. Normalized reaction enthalpy, ΔH_N° , for Reaction (1), as calculated by the PM3 method, versus calculated values of ΔH_N° from Eq. (3).

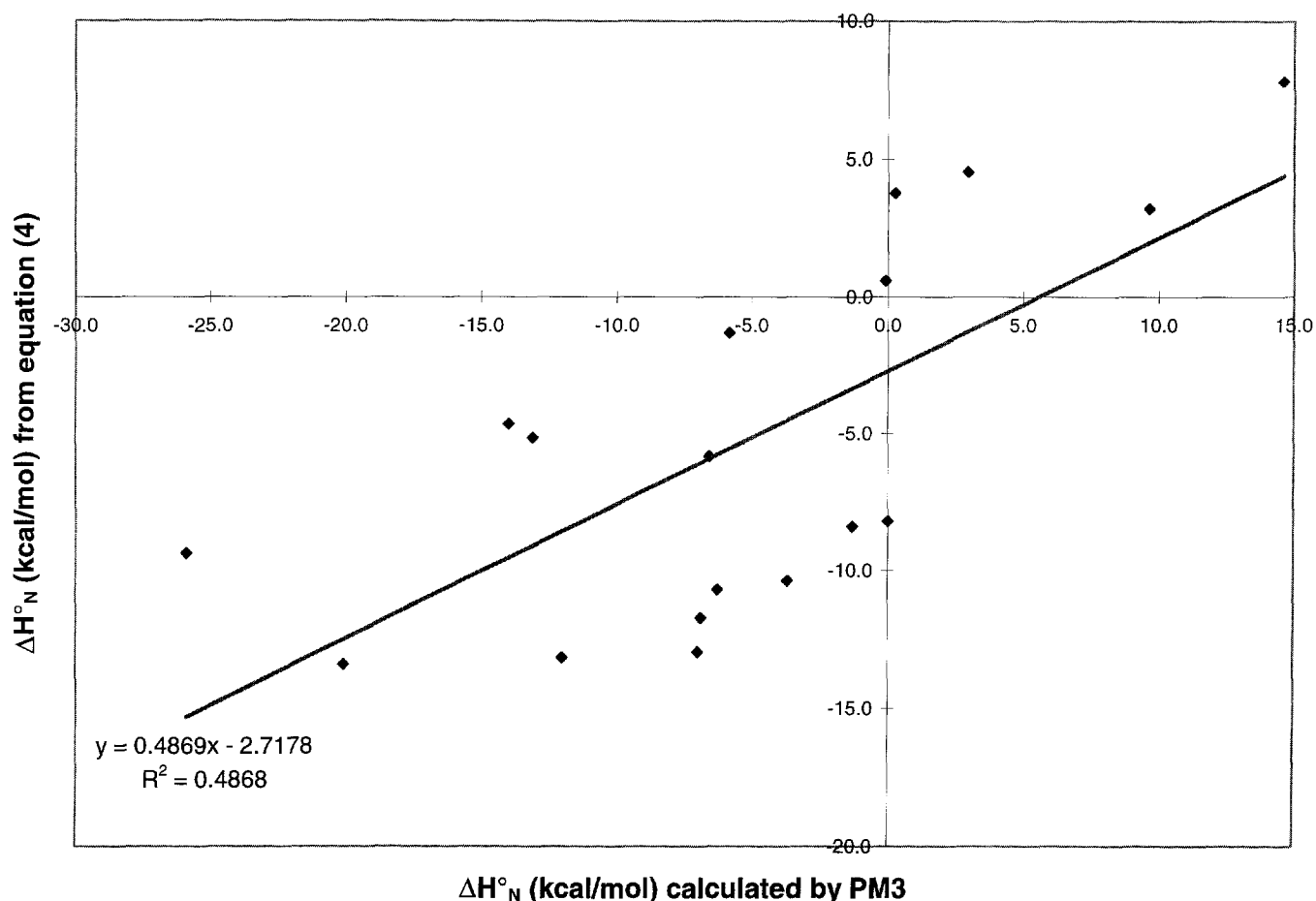


Figure 4. Normalized reaction enthalpy, ΔH_N° , for Reaction (2), as calculated by the PM3 method, versus calculated values of ΔH_N° from Eq. (4).

Table 3. Absolute deviation between enthalpies (Kcal/mol) of Reaction (1) calculated by the PM3 method relative to those obtained from Equation (3)

	ΔH_N° , Reaction (1)	Calculated ΔH_N°	Error	Absolute error
-Si(CH ₃) ₃	-14.1	-4.1	-10.0	10.0
-CH ₂ Si(CH ₃) ₃	-11.1	-8.2	-2.9	2.9
-C ₆ H ₅	-5.4	0.2	-5.5	5.5
-OCH(CH ₃) ₂	-5.2	0.9	-6.1	6.1
-N(CH ₃) ₂	-4.7	-7.7	2.9	2.9
-CH ₂ CH ₃	-3.0	-5.4	2.4	2.4
-OCH ₃	-2.7	-0.4	-2.3	2.3
-CH ₃	-2.3	-5.1	2.8	2.8
-NH ₂	-2.0	-7.5	5.5	5.5
-tBu	-1.6	-6.5	4.9	4.9
-OH	-1.1	-3.0	1.9	1.9
-H	0.0	-3.0	3.0	3.0
-SCH ₃	0.6	4.1	-3.5	3.5
-SH	4.8	5.9	-1.1	1.1
-Cl	7.7	9.9	-2.3	2.3
-I	9.5	9.1	0.4	0.4
-F	10.8	8.6	2.2	2.2
-CF ₃	20.7	13.1	7.5	7.5
			Average:	0.0
				3.7

Table 4. Absolute deviation between enthalpies (Kcal/mol) of Reaction (2) calculated by the PM3 method relative to those obtained from Equation (4)

	ΔH_N° , Reaction (2)	Calculated ΔH_N°	Error	Absolute error
-Si(CH ₃) ₃	-25.9	-9.4	-16.5	16.5
-CH ₂ Si(CH ₃) ₃	-20.1	-13.4	-6.7	6.7
-C ₆ H ₅	-14.0	-4.6	-9.3	9.3
-OCH(CH ₃) ₂	-13.1	-5.1	-8.0	8.0
-N(CH ₃) ₂	-12.0	-13.2	1.1	1.1
-CH ₂ CH ₃	-7.0	-13.0	6.0	6.0
-OCH ₃	-6.9	-11.7	4.8	4.8
-CH ₃	-6.6	-5.8	-0.7	0.7
-NH ₂	-6.3	-10.7	4.4	4.4
-tBu	-5.8	-1.3	-4.5	4.5
-OH	-3.7	-10.4	6.7	6.7
-H	-1.3	-8.4	7.1	7.1
-SCH ₃	-0.1	0.6	-0.7	0.7
-SH	0.0	-8.2	8.2	8.2
-Cl	0.3	3.8	-3.5	3.5
-I	3.0	4.6	-1.6	1.6
-F	9.6	3.2	6.4	6.4
-CF ₃	14.6	7.8	6.8	6.8
Average:			0.0	5.7

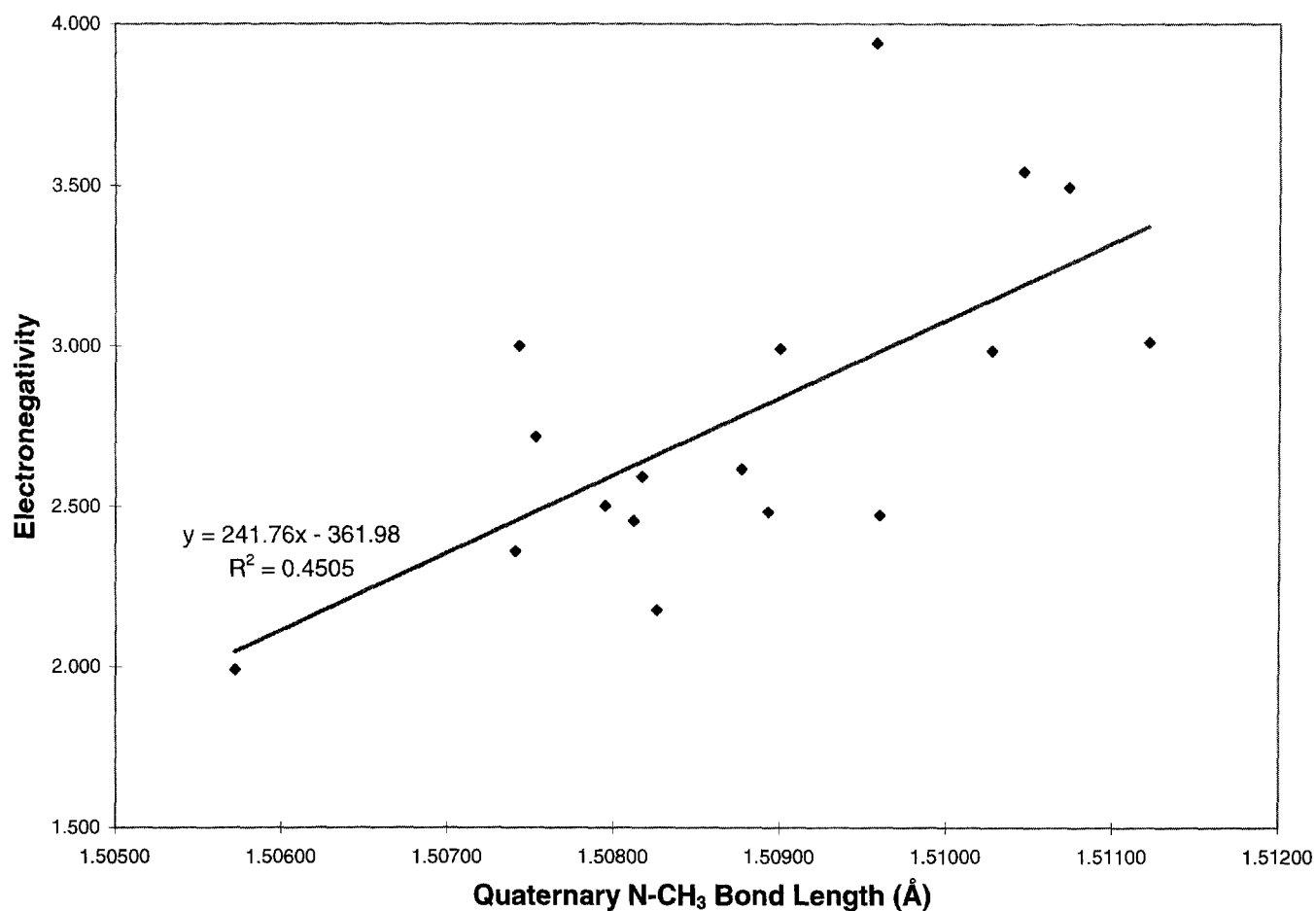


Figure 5. Substituent electronegativity versus quaternary N-CH₃ bond lengths of methyl-TEDA analogs.

Table 5. Standard enthalpies of formation for various iododalkanes, and enthalpies of reaction for quaternization of TEDA

Haloalkane (X) ^a	Standard formation enthalpies (kcal/mol)			Reaction enthalpies (kcal/mol)		Percentage removal efficiency ^b
	X	X-TEDA	X-TEDA-X	ΔH° , Reaction (1)	ΔH° , Reaction (2)	
CH ₃ CH ₂ I	2.0	155.9	398.0	86.8	174.9	95.31
CH ₃ I	9.4	162.4	414.5	85.9	184.9	98.82
CH ₃ CH ₂ CH ₂ I	-0.7	149.9	382.9	83.5	165.9	99.60
CH ₂ I ₂	33.5	194.4	474.9	93.8	213.4	99.95
C ₆ H ₅ I	44.6	192.3	461.9	80.6	202.4	99.99

Enthalpy of formation

Iodide	-64.625 kcal/mol
TEDA	2.508 kcal/mol

^a Haloalkanes sorted by percentage removal efficiency.

^b Percentage removal efficiency values taken from Freeman et al. (1986) [20].

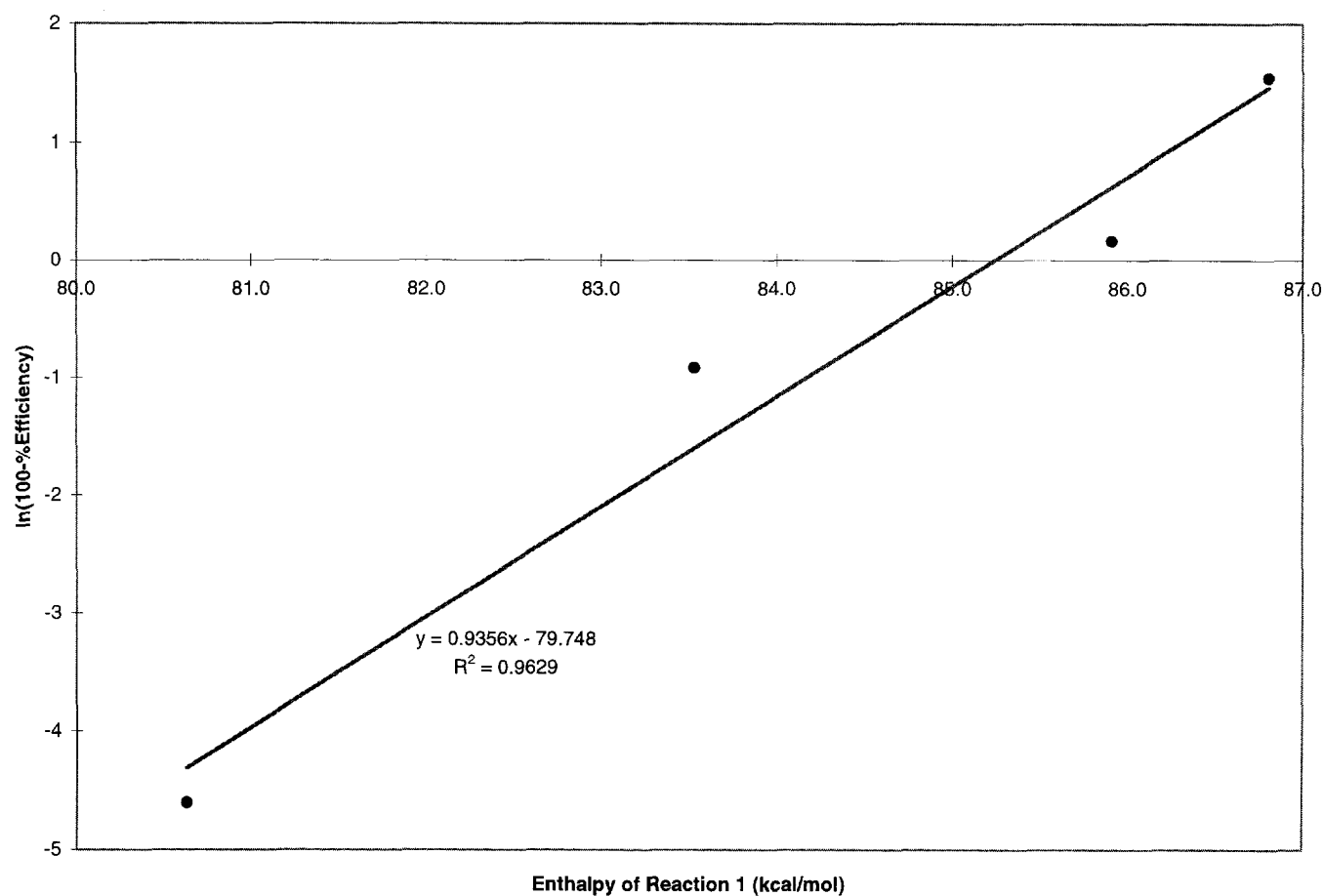


Figure 6. Filter efficiency versus monoquaternization enthalpies for reaction between TEDA and various organoiodides.

due to increased reactivity of this compound owing to steric factors as well as the presence of two electronegative elements attached to the central carbon. Examination of Figure 6 shows a clear correlation between calculated quaternization-reaction enthalpies and filter efficiency. This correlation results from the fact that reaction enthalpies for Reactions (1) and (2) affect the equilibrium between gas-phase and adsorbed iodine compounds (because the quaternary ammonium reaction products will be much less volatile than the gas-phase haloalkanes). Thus compounds that are only weakly chemisorbed spend a relatively large amount of time in the gas phase, and they have a correspondingly lower removal efficiency.

CONCLUSIONS

The results reported herein show that the PM3 semi-empirical method, as implemented in the HyperChem code, can be used to gain insight into the quaternization reactions that TEDA and its analogs undergo. Even though the PM3 semi-empirical method is a fairly modest computational procedure, it properly models both field and resonance components of the substituent effects in the TEDA quaternization reactions. Experimental thermodynamic data are not yet available for comparison, but it was possible to perform a linear regression of the field and resonance parameters for the substituent effects against calculated reaction enthalpy and obtain a statistically significant relationship. Such calculations can be used as a guide to estimate the reactivity of various TEDA analogs toward iodomethane. The PM3 method has been shown to be useful in estimating the removal efficiency by TEDA-impregnated charcoal filters for various organic iodides, other than iodomethane.

ACKNOWLEDGMENTS

This work was funded by AECL in the Underlying Chemistry Program. The authors appreciate critical review of this document by Joanna McFarlane and Clara Wren.

REFERENCES

- Rossin, J.A. and Morrison, R.W. Spectroscopic analysis and performance of an experimental copper/zinc impregnated, activated carbon. *Carbon* 1991, **29**, 887-892
- Capon, A., Alves, B.R., Smith, M.E., and White M.P. The adsorption of low boiling point gases by activated charcoal cloth. In: *Ext. Abstr. Program—Bienn. Conf. Carbon*, 15th, American Carbon Society, 1981, pp. 232-233
- Proceedings of the DOE/NRC Nuclear Air Cleaning Conference (19th), held in Seattle, Washington, August 18-21, 1986
- Lu, Y., Gao, J., Yin, Y., Wu, S., Bi, S., Lin, Z., Feng, Z., and Li, G. Cleaning iodine-131 in waste gases. I. Adsorption performance of various adsorbents for radioactive iodine and methyl iodide. *Yuanzineng Kexue Jishu* 1987, **21**, 167-172
- Moffett, R.B. Quaternary salts of triethylenediamine. *J. Med. Chem.* 1964, **7**, 450-453
- Pine, S.H., Cheney, J., Catto, B., and Petersen, J.D. Base-promoted reactions of bicyclic mono- and diquaternary ammonium salts. *J. Org. Chem.* 1974, **39**, 130-133
- Yakhontov, L.N. and Mrachkovskaya, L.B. 1,4-Diazabicyclo[2.2.2]octanes. *Khimiya Geterotsiklicheskikh Soedinenii* 1976, **6**, 723-738
- Hyder, M.L. Mechanisms of carbon aging and their effects on the retention of organic iodides by carbon. *Comm. Eur. Communities, [Rep.] EUR*, 1986, EUR-10580
- Broadbent, D. The aging and poisoning of charcoal used in nuclear plant air cleaning systems. *Comm. Eur. Communities, [Rep.] EUR*, 1986, EUR-10580
- Wren, J.C. and Moore, C.J. The effect of weathering on charcoal filter performance. I. The adsorption and desorption behavior of contaminants. *Nucl. Technol.* 1991, **94**, 242-251
- Wren, J.C. and Moore, C.J. The effect of weathering on charcoal filter performance. II. The effect of contaminants on the methyl iodide removal efficiency of triethylenediamine-impregnated charcoal. *Nucl. Technol.* 1991, **94**, 252-261
- Underhill, D.W. and Laskie, J.R. Modified TEDA impregnants for methyl iodide removal. In: *Proc. DOE Nucl. Air Cleaning Conf.*, 16th, U.S. Department of Energy, 1980, pp. 531-536
- Evans, M.G. and Hillary, J.J. Impregnants on charcoal for trapping methyl iodide: A further study of amines and quaternary salts. *Comm. Eur. Communities, [Rep.] EUR*, 1986, EUR-10580 pp. 525-545
- Stewart, J.J.P. Optimization of parameters for semi-empirical methods. II. Applications. *J. Comput. Chem.* 1989, **10**, 221-264
- Stewart, J.J.P. Optimization of parameters for semi-empirical methods. II Extension of PM3 to Be, Mg, Zn, Ga, Ge, As, Se, Cd, In, Sn, Sb, Te, Hg, Tl, Pb, and Bi. *J. Comput. Chem.* 1991, **12**, 320-341
- Swain, C.G., Unger, S.H., Rosenquist, N.R., and Swain, M.S. Substituent effects on chemical reactivity. Improved evaluation of field and resonance components. *J. Am. Chem. Soc.* 1983, **105**, 492-502
- March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*. John Wiley & Sons, New York, 1985, p. 17
- Inamoto, N. and Masuda, S. Revised method for calculation of group electronegativities. *Chem. Lett.* 1982. There is no "volume number" for Chem Lett, 1003-1006
- Gordy, W. A new method of determining electronegativity from other atomic properties. *Phys. Rev.* 1946, **69**, 604-607
- Freeman, W.P., King, M.P., and Kovach, J.L. In: *Proc. DOE/NRC Nucl. Air Cleaning Conf.*, 19th, U.S. Nuclear Regulatory Commission, Washington, DC, 1986, pp. 237-242.