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Estimation of Photolysis Lifetimes of the Nitronaphthalenes and Methylnitronaphthalenes

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The nitronaphthalenes (NNs) and the methylnitronaphthalenes (MNNs) in ambient atmospheres are largely formed from the atmospheric gas-phase formation from the parent PAHs by hydroxyl (OH) radical reactions during daytime and by nitrate (NO_3) radical reactions during nighttime in the presence of NO_x (Zielinska et al. 1989) and direct emissions from incomplete combustion processes (Wild et al. 1995; Bamford et al. 2003). Among nitropolycyclic aromatic hydrocarbons (nitro-PAHs), 1- and 2NN are the most abundant individual airborne nitro-PAHs. The concentration of them and the sum of their methyl-derivatives are reported to be several nanograms per cubic meter in ambient atmospheres (Arey et al., 1989). Some studies in recent years showed that most of NNs and MNNs are carcinogenic and genotoxic (Sasaki et al. 1997, 1999; Sauer et al. 1997). Therefore, it is of great importance to investigate their degradation in the environment in order to predict the risk to human health.

Photolysis is often suggested as the dominant atmospheric loss process for NNs and MNNs (Feilberg et al. 1999; Phousongphouang and Arey 2003). Photolysis lifetime (τ) is thus one of the most important parameters and is indispensable for environmental risk assessment of these volatile pollutants. However, little measured data are available regarding τ values of NNs and MNNs in ambient atmospheres because of large expenditures of money, time and equipment (Gupta et al. 1996; Dimashki et al. 2000; Feilberg and Nielsen 2001; Phousongphouang and Arey 2003). There is thus a need to develop quantitative structure-property relationship (QSPR) relating photolysis process data to other physicochemical properties or structural descriptors for enabling simple and fast estimation of photolysis process and generated predicted photolysis process data efficiently for these compounds. The aim of this study is to develop a reliable QSPR model for estimating τ values of NNs and MNNs and then extract the dominant effects on photolysis of NNs and MNNs under irradiation.

MATERIALS AND METHODS

Recently, the photolysis rates of 1NN, 2NN, and 11 MNNs were determined indoors using black-lamp irradiation and outdoors using natural sunlight by Phousongphouang and Arey (2003). Furthermore, the lifetimes of these

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compounds have been determined using a 12 h ambient average NO_2 photolysis rate value of 0.312 min^{-1}. The results from the experiment showed that the ambient lifetimes of these compounds ranged from 6 min for 1M8NN to 177 min for 2NN indoor and 9 min for 2M1NN to 293 min for 2M6NN outdoor, respectively. Due to the insufficient yields synthesis produced, measurements of 1M7NN, 2M3NN, 2M8NN were not determined. The results of photolysis rates to the NNs and MNNs are reproduced in Table 1. The 13 nitro-PAHs with τ values determined constitute the training set of the study. The three MNNs without experimentally determined τ values constitute the prediction set.

Table 1. The nitronaphthalenes and methylnitronaphthalenes under study and their atmospheric lifetimes, indoors*.

No.	Nitro-PAHs Name	Abbr.	τ (min) (*Obs.*)	logτ (*Obs.*)	logτ (*Pred.*)	*Diff.*	*SE*
1	1-nitronaphthalene	1NN	24	1.38	1.48	-0.10	±0.04
2	2-methyl-7-nitronaphthalene	2NN	177	2.25	2.08	0.17	±0.09
3	1-methyl-2-nitronaphthalene	1M2NN	31	1.49	1.68	-0.19	±0.04
4	1-methyl-3-nitronaphthalene	1M3NN	71	1.85	1.92	-0.07	±0.05
5	1-methyl-4-nitronaphthalene	1M4NN	22	1.34	1.30	0.04	±0.07
6	1-methyl-5-nitronaphthalene	1M5NN	38	1.58	1.38	0.20	±0.05
7	1-methyl-6-nitronaphthalene	1M6NN	88	1.94	1.98	-0.04	±0.05
8	1-methyl-8-nitronaphthalene	1M8NN	6	0.78	0.74	0.04	±0.11
9	2-methyl-1-nitronaphthalene	2M1NN	10	1.00	1.09	-0.09	±0.06
10	2-methyl-4-nitronaphthalene	2M4NN	41	1.61	1.58	0.03	±0.04
11	2-methyl-5-nitronaphthalene	2M5NN	49	1.69	1.58	0.11	±0.04
12	2-methyl-6-nitronaphthalene	2M6NN	133	2.12	2.10	0.02	±0.06
13	2-methyl-8-nitronaphthalene	2M8NN	31	1.49	1.60	-0.11	±0.05
14	1-methyl-7-nitronaphthalene	1M7NN			1.90		±0.06
15	2-methyl-3-nitronaphthalene	2M3NN			1.66		0.05
16	2-nitronaphthalene	2M7NN			2.16		±0.09

* *Obs.*: Observed values determined by Phousongphouang and Arey (2003); τ values of these compounds were determined using a 12 h ambient average NO_2 photolysis rate value of 0.312 min^{-1}; *Diff.*: difference between observed and predicted logτ values; *SE*: Standard errors for the predicted logτ values.

Quantum chemical descriptors computed by PM3 Hamiltonian can exactly describe the molecular properties, the PM3 is thus adopted to the quantum computation. A total of 14 descriptors reflecting the overall character of the nitro-PAHs were used in this study. A full list is given in Table 2. As the photolysis process proceeds in quite different ways depending on the surface and solution on/in which it takes place (Chen et al. 2001; Niu et al. 2004a, 2005), an adsorption related descriptor, *Mw*, was included. The parameter α indicates the ease with which species can be deformed by an electric field. Atomic charges are related to the reactive centers. The molecular orbital energies of a given molecule are related to chemical reactivity. Inductive effects and resonance effects exerted by the presence of different substituents and substructural groups within the molecule affect the electron distribution and stability of the molecular orbitals. Two non-empirical descriptors, ΔH_f and μ, are expected to reflect the affinity for leaching to some extent. The values of the selected molecular descriptors are summarized in Table 1 and the others for the studied compounds are available on request. In addition, three combinations of frontier molecular orbital energies, E_{LUMO}-E_{HOMO}, $(E_{LUMO}$-$E_{HOMO})^2$ and $E_{LUMO}+E_{HOMO}$, were also selected as predictor variables because many applications are available on the use of these parameters as quantum descriptors for developing QSPR models (Chen et al. 2001; Niu et al. 2004b). The E_{LUMO}-E_{HOMO} and $E_{LUMO}+E_{HOMO}$ can be related to absolute hardness and electronegativity respectively (Pearson 1986; Faucon et al. 1999).

Table 2. List of molecular structural descriptors of the nitronaphthalenes and methylnitronaphthalenes.

Symbols	Description
Mw	Molecular weight
ΔH_f	Standard heat of formation (kcal mol^{-1})
TE	Total energy (eV)
EE	Electronic energy(eV)
CCR	Core-core repulsion energy(eV)
E_{HOMO}	The energy of the highest occupied molecular orbital (eV)
E_{HOMO-1}	The energy of the second highest occupied molecular orbital (eV)
E_{LUMO}	The energy of the lowest unoccupied molecular orbital (eV)
E_{LUMO+1}	The energy of the second lowest unoccupied molecular orbital (eV)
Q_N^+	The largest positive atomic charge on a nitrogen atom (a.c.u)
Q_H^+	The most positive net atomic charges on a hydrogen atom (a.c.u)
Q_C^-	The largest negative atomic charge on a carbon atom (a.c.u)
μ	Dipole moment (a.u.)
α	Average molecular polarizability (a.u.)

QSPR models were developed using Partial Least Squares (PLS) analysis, as implemented in the Simca (Simca-S Version 6.0, *Umetri AB and Erisoft AB*) software. The conditions for the computation were based on the default options of the software. The criterion used to determine the model dimensionality - the number of significant PLS components - is cross validation (CV). The obtained QSPR model is considered to have a good prediction ability when the cumulative cross-validated regression coefficient (Q^2) for the extracted components, Q^2_{cum}, is larger than 0.5. Model adequacy was mainly measured as the number of PLS principal components (k), Q^2_{cum}, the correlation coefficient between observed values and fitted values (R), and the significance level (p). Besides the standard error of predicted values (*SE-Pred.*) given by PLS analysis, another standard error (*SE*) was adopted to assess the predictive power of the regression model. *SE* was defined like that in multiple regression analysis:

$$SE = \sqrt{\frac{\sum_{i=1}^{n}[\log \tau(\text{observed}))_i - \log \tau(\text{predicted})_i]^2}{n-k-1}} \tag{1}$$

Where logτ(observed) and logτ(predicted) are respectively the observed and predicted (over the test set) values of the dependent variable, and *n* stands for the number of observations used for model building in the training set.

RESULTS AND DISCUSSION

Table 1 shows different τ values under irradiation for different NNs and MNNs. The result indicates that τ values of NNs and MNNs in ambient atmospheres are affected by their molecular structures. Therefore, it is of interest to get the main factors affecting τ values of NNs and MNNs in atmospheric degradation under UV irradiation. In this study, PLS algorithm, not only finding the relationship between a matrix **Y** (containing dependent variables) and a matrix **X** (containing predictor variables) but also reducing the dimension of the matrices while concurrently maximizing the relationship between them (Chen et al. 2003; Niu and Yu 2004c), was applied to analyze photolysis of NNs and MNNs affected by different quantum chemical descriptors in the PLS model.

In a PLS model, Variable Importance in the Projection (*VIP*) is a parameter that shows the importance of a variable. Terms with large values of *VIP* are the most relevant for explaining dependent variable. Previous studies found that all predictor variables were not necessary for PLS modeling. To reduce the number of intercorrelated molecular structural descriptors, and to obtain an optimal model, the following PLS analysis procedure were adopted (Chen et al. 2003; Felipe-Sotelo et al. 2003). At first, a PLS model with all the predictor variables was calculated. Then the variable with the lowest *VIP* value was eliminated and a new PLS regression was performed, leading to a new PLS model. This procedure was repeated until the most important predictor variables were left. The optimal PLS model was selected with respect to the statistics Q^2_{cum}, R, p and SE.

The above described PLS analysis procedure with logτ as dependent variable and the 17 quantum chemical descriptors as independent variables, for the 13 nitro-PAHs contained in the training set, led to QSPR Model (1) as the optimal one for the photolysis lifetimes of different NNs and MNNs in the indoor experiments. The molecular descriptors selected in Model (1) were used to build Model (2) for the photolysis lifetimes of different NNs and MNNs in the outdoor experiments. The concrete results for models (1) and (2) are shown in Table 3. In Table 3, $R^2_{\mathrm{X(adj)(cum)}}$ and $R^2_{\mathrm{Y(adj)(cum)}}$ stand for cumulative variance of all the X's and Y's explained by all extracted components respectively, *Eig* stands for the eigenvalue that denotes the importance of the PLS principal components. It thus can be seen from Table 3 that the one PLS principal component was selected in Model (1), which explained 61.6% of the variance of the predictor variables, and 90.7% of the variance of the dependent variable. Table 4 lists *VIP* values in Models (1) based on the data in the indoor chamber with black-lamp irradiation and Model (2) based on the data in the outdoor chamber with sunlight irradiation.

As shown by Table 3, for the 13 NNs and MNNs contained in the training set, the correlation between observed and predicted logτ values is very significant in

Table 3. Model fitting results for Model (1) based on the data in the indoor experiments and Model (2) based on the data in outdoor experiments.

Models	k	$R^2_{X(adj.)(cum)}$	$R^2_{Y(adj.)(cum)}$	Eig	Q^2_{cum}	R	P	SE
Model (1)	2	0.455 0.616	0.830 0.907	3.000 1.041	0.789 0.843	0.960	<0.0001	0.126
Model (2)	2	0.437 0.587	0.624 0.779	2.936 1.032	0.515 0.684	0.903	<0.0001	0.200

Model (1) (R = 0.960, p<0.0001) and in Model (2) (R = 0.903, p<0.0001). As the cross-validated Q^2_{cum} value of these two models are remarkably larger than 0.50, these models are surely robust and show good prediction capability. Nevertheless, Table 3 shows that the Q^2_{cum} value of Model (1) is larger than that of Model (2). Thus Model (1) is more stable than Model (2). This may be reasonable since the change of light intensity and ambient temperature in outdoor experiments is larger than that in indoor experiments. Therefore the value of the outdoor photolysis experiments may overestimate such uncertainties and Model (1) derived from the indoor measurements are preferred. This model may be used to make prediction for other nitro-PAHs. Based on Model (1), τ values for the other 3 MNNs were predicted (Table 1). The predictions may give an initial estimation of photolysis lifetimes of NNs and MNNs in ambient atmospheric degradation.

Table 4 The PLS weights (W^*[1] and W^*[2]) and VIP values in models (1) and (2).

Variables	Model (1)			Model (2)		
	VIP	W^*[1]	W^*[2]	VIP	W^*[1]	W^*[2]
E_{LUMO}	1.199	*0.547*	*0.815*	1.274	0.454	0.886
CCR	1.104	*-0.546*	-0.070	1.098	-0.560	-0.154
ΔH_f	1.018	*-0.487*	-0.007	0.986	-0.469	0.182
Q_C^-	0.820	-0.202	*0.617*	0.784	-0.356	0.294
Q_N^+	0.796	0.352	-0.191	0.765	0.365	-0.322

There are totally five predictor variables included in these two models, respectively. VIP values for the variables are listed in Table 4. Based on the pseudo-regression coefficients of the independent variables and constants transformed from PLS results, analytical QSPR equation for Model (1) can be obtained, as follows:

$$\log\tau = -6.060 - 1.345\times10^{-2}\Delta H_f + 3.227E_{LUMO} + 4.573Q_N^+ - 0.701Q_C^- - 9.050\times10^{-3}CCR \qquad (2)$$

n=13, Q^2_{cum}=0.843, R=0.960, p=1.889×10^{-7}, SE=0.126

The effects of each independent variable on the logτ values of nitro-PAHs can be evaluated from the positive and negative symbols of the coefficients of the independent variables. From the PLS weights W^*[1] listed in Table 4, it can be seen how much a single variable contributes in each PLS component to the modeling of the logτ. The first PLS component is mainly related to the descriptor E_{LUMO}, CCR, and ΔH_f. The absolute values of W^*[1] for these descriptors are larger than 0.480 and larger than the absolute values of $W^*[1]$ for the other descriptors. As indicated by the pseudo-regression coefficients for the molecular structural descriptors, increasing CCR and ΔH_f values of the nitro-PAHs leads to decrease of $\log\tau$ values. Increasing E_{LUMO} values of the NNs and MNNs leads to increase of $\log\tau$ values. The descriptor E_{LUMO} indicates the ability of the molecule to accept electrons from others in the process of photolysis. Thus the lower the value of E_{LUMO} is, the more probable the molecule accepts electrons. This study indicates that the compound with lower E_{LUMO} value will be easier to be photodegraded.

The second PLS component is loaded primarily on descriptor E_{LUMO} and Q_C^-, for which the two $W^*[2]$ values are larger than 0.610 and larger than the absolute values of $W^*[2]$ for the other descriptors. It can be found from Eq. (2) that increasing Q_C^- values of the nitro-PAHs leads to decrease of $\log\tau$ values. Q_C^- may characterize atomic charges, which are related to the reactive centers of nitro-PAHs molecular. The higher Q_C^- values the lower respective $\log\tau$ values of NNs and MNNs in ambient atmospheres under irradiation, which is consistent with the result from Niu et al. (2004b), who found that the higher the charge distribution for carbon, the easier for photodechlorination to occur. In addition, Eq. (2) also suggests that the higher Q_N^+ value for a nitro-PAH molecule the longer photolysis lifetime.

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