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Project Summary

Structure-Reactivity Relationships for Predicting Environmentally Hazardous Chemicals

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A method previously developed for extrapolating rate coefficients by conventional transition-state theory was applied to reactions of hydroxyl (OH) radicals with 10 halomethanes and 18 haloethanes. For each reagent, the entropy of activation $\Delta S^{\ddagger}$ was calculated. That value, together with an experimental value of the rate of reaction at 298 K, k(298), was used to calculate k(T) at higher temperatures. The calculated values for all the haloalkanes differed from experimental values by no more than 25%, except that of (OH + $CHCl_3$), for which the possibility of experimental errors was considered.

Those calculations were then used to develop a simpler, approximate scheme that can be applied to any haloalkane. For α-hydrogen abstraction reactions, $\Delta S^{\ddagger}(298)$ can be fitted, with a maximum error of 1.4 and an average error of 0.3 cal mol^{-1} K^{-1} (entropy units, or eu), by

$$\Delta S^{\ddagger}(298) = -2.2 \ln M - 18.0 + R \ln n_H$$

where M = molecular weight of the haloalkane and n_H = the number of abstractable α-hydrogen atoms. The activation energy at 298 K, E(298), can be fitted, with an average error of 0.3 and a maximum error of 1.1 kcal/mol, by

$$E(298)/R = 2100 - 85n_F - 51n_{Cl} - 950n_{CH_3} - 600n_{CH_2X} - 650n_{CHX_2} - 250n_{CX_3}$$

where the n_i indicate the number of H atoms on CH_4 replaced with the indicated substituents, and X is either Cl or F. The above relations for $\Delta S^{\ddagger}(298)$ and E(298) are used to generate a "universal" rate coefficient expression that depends only on the molecular weight and the number of abstractable H atoms in the reagent haloalkane:

$$k(T) = n_H\, 10^{6.5}\, M^{-1}\, T^{1.5} \exp[-[E(298)/R - 450]/T]$$

where E(298)/R is given by the preceding equation. For most reagents, this expression predicts rate coefficients within a factor of 3 of experimental data and provides a useful predictive tool if no reliable data are available.

This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The aim of this research has been to develop the means for predicting reactivities of potential man-made pollutants in the stratosphere and troposphere. Although it is possible to measure reactivities in the laboratory, the number of possible species of concern is enormous, and the cost of studying each one in detail would be prohibitive. The assessment of the atmospheric fate of pollutants can, for the most part, be satisfied by a procedure that enables prediction of reactivities to within a factor of 3 to 5, without requiring the higher accuracy attainable by elaborate laboratory measurements.

Consideration of the important oxidizing species in the atmosphere and their relative reactivities leads to the conclusion that for almost all reagents, the species that determines the lifetime of an atmospheric pollutant is the hydroxyl (OH) radical. Consequently, any program concerned with predicting reactivities of potential pollutants should concern itself first with the reactions of OH radicals. For this reason, the work under this contract focused on OH reactions.

The initial efforts proceeded in two phases: The first addressed the problem of calculating in detail the temperature dependence of the reaction rate coefficients; the second explored the possibility of developing simplified procedures for estimating, with sufficient accuracy, the rate coefficients of OH reactions at any temperature. The second phase required estimating both the entropy of activation ($\Delta S^{\ddagger}$), and, with more difficulty, the energy of activation (E). These two parameters determine the rate of reaction at any temperature, in accordance with the general equation

$$k(T) = C \exp(\Delta S^{\ddagger}/R) \exp(-E_a/RT) \quad (1)$$

Finally, the problem of developing a universal rate coefficient expression that can predict with reliability the rate coefficients, at various temperatures, for reactions of OH radicals with important atmospheric pollutants was addressed.

Procedure

Transition-State Theory Calculations

The procedure follows our previous studies. Here, the general reaction is

$$XYZCH + OH \rightarrow \begin{matrix} X \\ \diagdown \\ Y\text{--}C\text{--}H \\ \diagup \\ Z \end{matrix}^{\prime} \quad \begin{matrix} O \\ \diagdown \\ H \end{matrix}^{\prime} \rightarrow$$

$$XYZ\dot{C} + HOH$$

where X, Y, and Z are each either H, Cl, F, CH_3, or a halomethyl radical. The principal problem is how to calculate the entropy of the activated complex, $S^{\ddagger}$. The calculation involves using the haloalkane reagent RH itself as a model compound, then making suitable corrections to the various degrees of freedom as indicated below. The entropy $S^{\ddagger}$ is then given by

$$S^{\ddagger} = S^{\circ}_{RH} + \Delta S_t + \Delta_v + \Delta S_r + \Delta S_{ir} + \Delta S_e + \Delta S_\sigma + \Delta S_n \quad (2)$$

where the ΔS terms represent the corrections required in replacing the properties (translation, vibration, rotation, internal rotation, electronic, symmetry, optical isomerism, respectively) of the model compound by those of the activated complex.

It was assumed that the C·H, H·O, and O-H bond lengths and C·H·O and H·O-H bond angles are approximately the same as those calculated by Walch and Dunning[1] for the reaction of (OH + CH_4): 1.2, 1.3, 1.0 Å and 160° and 110°, respectively. From this information, the product of moments of inertia of the complex $I^{\ddagger}$ can be calculated, whence $\Delta S_r = R \ln (I^{\ddagger}/I)$, where I is the product of the moments of inertia of the reagent RH. ΔS_t is given by $(3/2)\ R \ln(M^{\ddagger}/M)$. The electronic degeneracy of the activated complex is assumed to be 2, whence $\Delta S_e = R \ln 2 = 1.38$ eu (entropy units, or cal $mol^{-1}\ K^{-1}$). $\Delta S_\sigma = R \ln(\sigma/\sigma^{\circ})$, where σ abd $\sigma^{\ddagger}$ are the external symmetry numbers of the alkane and complex, respectively, calculated assuming rigid rotation. $\Delta S_n = R \ln (n^{\ddagger}/n)$, where n and $n^{\ddagger}$ are the numbers of optical isomers in the alkane and complex, respectively. Only the vibrational frequencies and internal rotations of the activated complex remain to be determined.

Vibrational Frequencies

For each halomethane XYZCH, where X, Y, and Z are either H, Cl, or F, we estimated the vibrational frequencies in the activated complex by using those in the molecule XYZCF as guides, on the assumption that the C·H·OH portion of the activated complex is similar to the C-F portion of a real molecule. The vibrational-frequency changes in the activated complexes for all the halomethanes are summarized in the full report.

For the haloethanes, it was not possible to examine each reaction in detail because there are more frequencies, fewer mode identifications, and fewer molecules for which detailed spectra are available. Instead, the vibrational frequencies of CH_3CH_3, CH_3CH_2F, CH_3CHF_2, and CH_3CF_3 were compared, the change in the first pair representing the reaction of OH with all haloethanes with only β-hydrogen atoms (i.e., no H atoms on the same C atom as F or Cl atoms), and the changes between the second and third pairs representing reactions with α-H atoms. Because the experimental data indicate that a reaction with haloethanes containing only β-H atoms is at least an order of magnitude slower than for haloethanes with some α-H atoms, it was assumed that in those reagents containing both α- and ν-H atoms, the reaction with the β-H atoms could be neglected. In both kinds of reactions, it was assumed that the newly formed C·H·O and H·O-H bonds have the same values that were used in the halomethane reactions (1000 cm^{-1} each).

Internal Rotations

The properties of the internal rotations must be evaluated accurately, because considerable entropy is associated with these two degrees of freedom. The moments of inertia for the internal rotations are calculated by the procedure of Herschbach et al.[2] The entropy of free rotation is given by $S_f = R(\ln Q + 1/2)$, where $Q = 0.35(I_r T)^{1/2}/\sigma$ for I_r, the reduced moment of inertia, in dalton-Å. Here σ is the symmetry of the internal rotation, which is 1 for most of the reagents considered in this report but 3 for rotation about the C-H bond in CH_4, $CHCl_3$, and CHF_3. For rotation about the C·H bond, $Q \approx 6.2/\sigma$ for all halomethanes and 1.8 for CH_4. For rotation about the O·H bond, $Q \approx 5.9$ for all halomethanes and 5.1 for CH_4. The corrections to the entropy due to the barrier to rotation, $S_t - S_h$, are interpolated from tables developed by Pitzer and coworkers where S_h = entropy of hindered rotation.

For all the haloethanes, the reduced moment of inertia I_r for rotation about the C·H bond is approximately 1.1 dalton-Å, which makes the partition function Q equal to 6.5, and the entropy of free rotation S_f, 4.7 eu. For rotation about the H·O bond, $I_r = 0.95$, $Q = 6.0$, and $S_f = 4.6$ eu.

Unlike the halomethanes, the haloethanes already have one internal rotation — about the C-C bond. In a previous study involving transition-state theory calculations for reactions of oxygen (O) atoms with alkanes, reasonable agreement with experiment was obtained by assuming that the barrier to internal rotation was lowered by 1 kcal/mol in the activated complex. The same assumption was made here. The contributions to $\Delta S^{\ddagger}$ are shown in the full report. There is a qualitative difference between the reactions abstracting α-H atoms and those abstracting β-H atoms, because the OH adduct makes a much greater change in the moment of inertia of a CH_3 group than it does when added to a halomethyl group.

[1] Walch, S. P., and T. H. Dunning, Jr. J. Chem. Phys., 72:1303, 1980.

[2] Herschbach, D. R., H. S. Johnston, K. S. Pitzer, and R. F. Powell. J. Chem. Phys., 25:736, 1956.

Empirical Correlations

The results of the detailed transition-state theory calculations outlined above were used to establish simple empirical correlations between activation entropy and activation energy for an arbitrary (OH + haloalkane) reaction with readily determined molecular parameters. The following procedure generates simple, approximate expressions for $\Delta S^{\ddagger}(298)$ and for E(298) without requiring more information than the molecular weight of the reacting haloalkane and its gross structural details.

Entropy of Activation

The entropy of the activated complex, $S^{\ddagger}$, is calculated from the entropy of the reacting haloalkane RH by a series of corrections terms:

$$S^{\ddagger} = S^{\circ}_{RH} + \Delta S_t + \Delta S_v + \Delta S_r + \Delta S_{ir} + \Delta S_e + \Delta S_\sigma + \Delta S_n \quad (3)$$

where the ΔS terms represent the corrections required in replacing the properties (translation, vibration, rotation, internal rotation, electronic, symmetry, optical isomerism, respectively) of the haloalkane by those of the activated complex. The translational contribution ΔS_t is given by $(3/2)R \ln(M^{\ddagger}/M)$; therefore, it will decrease to zero as the mass M of the reagent RH increases (since $M^{\ddagger} = M + M_{OH}$). The rotational contribution ΔS_r is given by $(1/2)R \ln[(I_aI_bI_c)^{\ddagger}/(I_aI_bI_c)]$, where the three I factors are the principal moments of inertia. Each I depends approximately on M; hence ΔS_r too will decrease to zero as the size of the reagent haloalkane (and hence its molecular weight) increases. The vibrational contribution, ΔS_v, is the sum of contributions from each vibrational mode, each of which varies approximately with vibrational frequency. In this procedure, several vibrational modes, all of comparable frequencies in different reagents, are replaced by other modes in the activated complexes, for which the frequencies are comparable for different reactions. A similar argument, though somewhat weaker, can be made for internal rotations. The remaining three terms on the right-hand side of Eq. (3) are independent of mass. These arguments suggested that there might be some correlation between $\Delta S^{\ddagger}(298)$ and M, a suggestion borne out by graphic display of the data.

Activation Energy

Previously, workers attempted to correlate activation energies with bond dissociation energies (BDEs) of the dissociating bond. This approach was tried with moderate success for (OH + halomethane) reactions. However, the same could not be done profitably for the haloethanes because BDEs are known for very few of the compounds. Instead, an empirical correlation was made of the activation energies with a set of six structural parameters; each parameter describes the correction to the activation energy of CH_4 that must be made as H atoms are substituted by F, Cl, CH_3, CH_2X, CHX_2, or CX_3, where X = F or Cl. (At present there are temperature-dependent rate data for only one brominated haloalkane; hence, attention was confined to fluorinated and chlorinated compounds until more data become available.) In other words,

$$E(298)/R = E(CH_4)/R - a_F n_F - a_{Cl} n_{Cl} - a_{CH_3} n_{CH_3} - a_{CH_2X} n_{CH_2X} - a_{CHX_2} n_{CHX_2} - a_{CX_3} n_{CX_3} \quad (4)$$

The calculated activation energies for all halomethanes and haloethanes (except CHF_3 and CH_3CF_3, which pose unique problems), which are derived from the experimental values of k(298), were used in deriving the values of the various a_i. The results of this effort are given in the following section.

Results and Discussion

Transition-State Theory Calculations

OH + Haloalkanes

Transition-state theory calculations were carried out using the vibrational-frequency changes and the entropies of activation listed in the full report. There it was shown that the temperature exponents n for all the α-hydrogen abstractions are 1.6 to 1.7, whereas for the three β-hydrogen abstraction reactions n = 1.1. For the halomethanes, two models were used for each reaction: one with hindered internal rotation, and one with free internal rotation. The two models were otherwise identical. On the average, the free internal rotation model appears to give slightly better agreement with the data. For all but one reagent, agreement with experimental data is within the experimental uncertainties, and discrepancies between experimental and calculated rate coefficients are no greater than 25%.

The single puzzling exception is $CHCl_3$, for which both models greatly underpredict the activation energy and hence the rate coefficients at $T > 300$ K. To obtain agreement with the data requires a greatly increased $\Delta S^{\ddagger}(298)$ — from -28.7 to ~-25.3 eu — for the free internal rotation case. One way to achieve this is by lowering the four low-frequency vibrations in the activated complex to 150 cm^{-1}. However, there is no *a priori* reason for making the frequencies of this one complex so much lower than those of all the others.

The discrepancy between the calculated and experimental values of k(T) for this halomethane suggests either that k(300) is really larger than the measured value or, more likely, that at higher temperatures (400-500 K), another process removing OH radicals is occurring. Because of the possible serious consequences for the applications of the thermochemical approach to conventional transition-state theory as we have been using it, we recommend that the (OH + $CHCl_3$) reaction rate be carefully remeasured over a temperature range sufficiently wide to eliminate any doubts concerning both the absolute value of the rate coefficients and the activation energy.

Empirical Correlations

Activation Entropies

In the full report, $\Delta S^{\ddagger}(298)$ for the free internal rotation model is plotted against the molecular weight M of the reacting haloalkane for all the α-hydrogen abstractions. The least-squares fit through all the points is described by

$$\Delta S^{\ddagger}(298)\ (\text{eu/H atom}) = -2.2 \ln M - 18.0 \quad (5a)$$

or

$$\Delta S^{\ddagger}(298) = -2.2 \ln M - 18.0 + R \ln n_H \quad (5b)$$

where S is in eu (entropy units, or cal mol^{-1} K^{-1}), M is in daltons, and n_H is the number of abstractable α-H atoms. This expression fits all the data with a maximum error of 1.4 eu and an average error of 0.3 eu. [The values of $\Delta S^{\ddagger}$ **for CH_3CCl_3, CH_3CF_3, and CH_3CF_2Cl, which have only β-H atoms,** are all 2 to 3 eu larger than Eq. (2) predicts.] When M becomes large enough (approximately 220 daltons), the contributions to ΔS_t and ΔS_r **will be close to zero, and** $\Delta S^{\ddagger}(298)$ per H atom should reach a minimum value of ~-30.3 eu.

Activation Energies

Using the approach outlined above, a least-squares fitting program was applied to activation energies for 28 (OH + haloalkane) reactions to solve for the parameters a_i of Eq. (4). The derived

values, based on $E(CH_4)/R = 2100$ at 298 K, are:

$a_f = 85$ $a_{CH_2X} = 600$
$a_{Cl} = 515$ $a_{CHX_2} = 650$
$a_{CH_3} = 950$ $a_{CX_3} = 250$

The values of E(298)/R predicted with Eq. (4) are compared with the experimentally derived values in the full report. The discrepancy between predicted and derived values is never worse than 570, i.e., an error in E of 1.1 kcal/mol, and in most casts is considerably smaller: The average error is 150, i.e., 0.3 kcal/mol.

This approach to calculating the energetics of a reaction is not novel: It relies on what is essentially a bond additivity argument. Heicklen[3] explored a similar approach to predicting BDEs, from which he predicted rate coefficients for reactions of OH radicals with a wide variety of organics. The difference here is the use of the approach directly for calculating activation energies, rather than BDEs. This shortcut circumvents the problem of the uncertainties in many BDEs — generally 1 to 2 kcal/mol. These uncertainties may introduce errors into the bond additivity expressions for predicting unmeasured BDEs and hence in activation energies. Since the correlation factor in the equation relating activation energies with BDEs is approximately 0.4, a 2-kcal/mol error in BDE imparts an error to k(298) of a factor of 3.8.

A "Universal" Rate Coefficient Expression

Equation (4) for E(298)/R and Eq. (5) for $\Delta S^{\ddagger}(298)$ can be substituted in the general expression for k(T) from transition-state theory to yield a general rate coefficient expression for (OH + haloalkanes) that depends only on the molecular weight of the reagent and the number of various substituents. We can force a $T^{1.5}$ pre-exponential temperature dependence to agree with the results of the calculations. The A factor is determined by requiring the expression to yield the proper values of k(298) and E(298). The result is

$$k(T) = n_H\, 10^{6.5}\, M^{-1}\, T^{1.5} \exp(-B/T) \quad (6)$$

where M is in daltons and T is in kelvins. The pre-exponential factors have been modified slightly to round off the exponent of the molecular-weight factor M. The term B is calculated from E(298)/R obtained from Eq. (4): B = [E(298)/R - 450]. The rate coefficients resulting from Eq. (6) are shown for several typical reactions in figures given in the full report. [Equation (6) does not apply to haloethanes with only β-hydrogens.] For $CH_2ClCHCl_2$ and CH_2FCHF_2, Eq. (6) was applied separately to the two different kinds of H atoms and the results summed together. In general, the rate coefficients calculated by Eq. (6) disagree with experimental data (where they exist) by less than a factor of 3.

Conclusions

Four principal conclusions emerge from the present study. The first is that a reasonable set of assumptions can be applied consistently to all but one of the reactions considered here to obtain transition-state models that lead to calculated rate coefficients in good agreement with experimental data. This is true even though the A factors at 298 K are not in particularly good agreement with experimental values. The good agreement is a result of the tendency of activation entropies and energies to compensate one another.

The second conclusion is that one of the reactions — that of ($OH + CHCl_3$) — is anomalous. Either the experimental data are flawed or there is something unusual about the dynamics of this reaction, requiring a qualitatively different activated complex to obtain agreement between calculations and experiments. A new experimental investigation is recommended.

Third, the above two conclusions together demonstrate that, while one might be able to tailor a model for the activated complex to force reasonable agreement with a particular set of experimental data for one reaction, simultaneous agreement with data for several homologous reactions is by no means a fortuitous achievement. The greater constraints imposed by treating an entire family of reactions together rather than a single reaction give greater confidence that the model and the resulting calculations are physically meaningful.

Finally, we used the calculations just discussed as a guide for generating empirical expressions for $\Delta S^{\ddagger}(298)$ and E(298) for α-hydrogen abstraction reactions of OH radicals from fluorinated and chlorinated methanes and ethanes. The calculated entropies and energies of activation were then applied to generate a "universal" rate coefficient that depends only on the molecular weight and the number of abstractable α-hydrogen atoms of the reagent haloalkane. This expression predicts rate coefficients within a factor of about 3 of the experimental data for all 26 reactions for which data were available (and generally much better), and offers promise as a predictive tool when no reliable experimental data are available.

[3] Heicklen, J. Int. J. Chem. Kinet., 13:651, 1981

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The complete report, entitled "Structure-Reactivity Relationships for Predicting Environmentally Hazardous Chemicals," (Order No. PB 87-140 497/AS; Cost: $9.95, subject to change) will be available only from:
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