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Regularities in Arrhenius parameters for rate constants of abstraction reactions of hydroxyl radical with C–H bonds

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Abstract

For compounds with a single type of C–H bond, it is shown that the Arrhenius parameters E/R and the A-factor for OH abstraction reactions can be reliably predicted from k(298 K), based on relationships derived from selected literature data. The principal criterion for selection is that the data shall have been verified by both absolute and relative rate measurements. Predictions are compared to tabulated data in recent NASA data evaluations, showing for the most part good agreement. In two of the cases where discrepancies exist, the OH reactions with CH_3CN and CF_3CH_2Cl (HCFC-133a), new relative rate data are presented which show improved agreement with predictions.

Keywords: Hydroxyl; Abstraction; CH_3CN; CF_3CH_2Cl

1. Introduction

There is now an extensive body of data for the rates of abstraction reactions by OH from hydrocarbons and halocarbons. From these data, two types of useful correlations can be made. The first is the effect of different substituent groups on the magnitudes of the rate constants. This approach, sometimes referred to as the structure–additivity-relationships (SAR) method [1], can often predict k(298 K) for the OH reactions within a factor of about 1.5–2, depending on the accuracy of the database used for calibration and other factors such as the number and type of groups attached to a given carbon atom in the molecule. The second, which is the main subject of this paper, is a correlation between k(298 K) and the quantities A and E/R in the two-parameter Arrhenius equation, $k(T) = Ae^{-E/RT}$. The pre-exponential factor A is normally given in units of $cm^3/(mol\,s)$, and the activation temperature E/R has the unit K. The quantity R is the gas constant, with the value 1.987 cal K^{-1} mol^{-1}. The two-parameter Arrhenius equation is appropriate only in the temperature range below about 450 K. At higher temperatures, a more complex temperature dependence becomes apparent, and a three-parameter expression such as $k(T) = A'T^n e^{(-E'/RT)}$ must be used. However, the bulk of reported kinetics data fall in the lower temperature region, and the two-parameter Arrhenius expression is an adequate representation of the data. At very low temperatures, other factors such as different reaction sites, possible tunneling, or experimental error may lead to appreciable curvature in a two-parameter Arrhenius plot.

Correlations of Arrhenius parameters with k(298 K) have been discussed previously [2,3], based on an observed dependence of the pre-exponential factors for OH reactions on the magnitude of k(298 K). Inclusion of the dependence of A-factors on the magnitude of the rate constant is an improvement over earlier rate constant estimates [4] in which a constant A-factor (per C–H) bond was assumed. Such an approximation is acceptable when the rate constants are of similar magnitude, but fails when they differ by a factor of ten or more. The present paper emphasizes the relationship between E/R values and k(298 K), an approach which further demonstrates that pre-exponential factors per C–H bond increase systematically with increasing k(298 K). The correlation between k(298 K) and the Arrhenius parameters is sufficiently accurate that temperature dependence studies below about 450 K for reactions with compounds having only one type of C–H bond are unnecessary

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Table 1
Selected data for OH abstraction reactions for calibration of the relationship between E/R values and k(298 K)

Compound	Temperature range (K)[a]	A-factor (cm^3/(mol s))	E/R (K)	k(298 K) (cm^3/(mol s))	Reference
CH_3CFCl_2 (141b)	287–393	1.71×10^{-12}	1699	5.71×10^{-15}	Talukdar et al. [20]
CHF_2Br (22B)	233–432	1.11×10^{-12}	1405	9.98×10^{-15}	Talukdar et al. [21]
CHF_2Cl (22)	298–460	7.76×10^{-13}	1495	5.14×10^{-15}	Orkin and Khamaganov [22]
CH_2F_2 (32)	222–381	1.66×10^{-12}	1487	1.13×10^{-14}	Talukdar et al. [20]
CF_3CH_3 (143a)	296–374	1.2×10^{-12}	2024	1.34×10^{-15}	Talukdar et al. [20]
CF_3CH_2F (134a)	273–450	1.34×10^{-12}	1690	4.60×10^{-15}	Gierczak et al. [23]
CF_2ClCCl_2H (122)	298–460	1.21×10^{-12}	942	5.14×10^{-14}	Orkin and Khamaganov [22]
CH_3Br	273–379	2.38×10^{-12}	1310	2.93×10^{-14}	Mellouki et al. [24]
CH_3OCH_3	263–364	1.51×10^{-11}	496	2.86×10^{-12}	DeMore and Bayes [25]
c-C_6H_{12}	225–408	3.10×10^{-11}	471	6.38×10^{-12}	Wilson et al. [26]
c-C_5H_{10}	209–407	2.67×10^{-11}	509	4.84×10^{-12}	Wilson et al. [26]
c-C_3H_6	272–463	7.28×10^{-12}	1356	7.68×10^{-14}	Wilson et al. [26]
c-C_4H_8	272–366	1.62×10^{-11}	611	2.09×10^{-12}	DeMore and Bayes [25]
CH_4	n/a	2.45×10^{-12}	1775	6.34×10^{-15}	JPL 97-4 [5]
CH_3CH_3	n/a	8.70×10^{-12}	1070	2.40×10^{-13}	JPL 97-4 [5]

[a] Temperature range in which data were fit.

in most cases, a single measurement at 298 K being sufficient.

Rate constant evaluations such as NASA/JPL 97-4 [5] and 02-25 [6] are averages or fits to all reported data which are not clearly erroneous, without compelling regard for estimations or expected Arrhenius parameters. It is shown in the present analysis that such recommendations are generally accurate, although in a few cases errors are apparent. For two such cases, the OH abstraction reactions with CH_3CN and CF_3CH_2Cl (HFC-133a), previously unpublished data are presented which show better agreement with expectations.

2. Methods

2.1. Calibration of the relationship between k(298 K) and the Arrhenius parameters

Table 1 shows a selection of rate constant data for OH abstraction reactions covering three orders of magnitude in k(298 K). It is important to note that each compound has C–H bonds of only one type. This requirement avoids ambiguity arising from the presence of different reaction sites with different rate parameters. The data are taken from several laboratories and were chosen for the most part by the requirement that they have been verified by both absolute and relative rate measurements. The set is not unique, but inclusion of other data meeting the same criteria would not change the result significantly.

2.2. Relative rate measurements for CH_3CN and CF_3CH_2Cl

The method used here for the relative rate measurements has been described in detail previously [3]. It consists of a slow-flow photolysis apparatus in which OH is produced by photolysis of ozone in the presence of water vapor, and in which reactant concentrations and losses are measured by FTIR spectroscopy.

The reference gases for CH_3CN and CF_3CH_2Cl were methane and methyl chloroform, respectively. The reference rate constants are shown in Table 2.

3. Results

3.1. Relationship between k(298 K) and the Arrhenius parameters

The rate constants k(298 K) must be normalized to a per-hydrogen basis in order to account for the fact that many compounds have more than one C–H bond. Fig. 1 is a graph of such data from Table 1, showing a linear relationship between the E/R values and k(298 K)/n for both hydrocarbons and halocarbons, where n is the number of H-atoms. From a fit to the data,

$$\frac{E}{R}\,(\mathrm{K}) = (-509.05 \pm 8.65)\log_{10}\left(\frac{k_{298\,\mathrm{K}}}{n}\right) - (5771.2 \pm 119.2) \quad (1)$$

Table 2
Rate constants for the reference compounds used in this work for relative rate studies[a]

Reference compound	A-factor (cm^3/(mol s))	E/R (K)	k(298 K) (cm^3/(mol s))	Source
Methane	$(2.45 \pm 0.25) \times 10^{-12}$	1775 ± 50	6.34×10^{-15}	JPL 97-4 [5]
Methyl chloroform	$(2.02 \pm 0.25) \times 10^{-12}$	1608 ± 50	9.15×10^{-15}	Talukdar et al. [27][b]

[a] Uncertainties in the Arrhenius parameters are our estimates (1 sigma).
[b] Rate parameters derived from fit to data at 295–379 K.