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Interactive comment on "Kinetics of the gas-phase reactions of OH radicals with alkanes and cycloalkanes" *by* R. Atkinson

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I thank the reviewers for their very useful comments. The more extensive comments of Referee 1 also include those of R. Cox (Editor), and hence the comments of Referee 1 are responded to, as follows:

I agree with the suggestion of both reviewers that a Summary Table be included, and this is now Table 1.

The recommendations are given for the temperature ranges over which the rate data used in the evaluation were obtained. In certain cases (for example, methane-d_2, methane-d_3, n-hexane and 2,3-dimethylbutane) use of the recommended rate expressions outside of these temperature ranges is liable to lead to significant uncertainties (and probably errors). For those alkanes and cycloalkanes with recommended rate

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expressions using the three-parameter fit $k = AT^n e^{-B/T}$, use of the recommended rate expression at higher and lower temperatures than the cited temperature range is reasonable, recognizing that the uncertainties will be larger the further away from the temperature range cited in the recommendation.

As expected, the error limits at temperatures other than 298 K depend on the quantity and quality of the data at those temperatures, and for the larger alkanes the data base at temperatures other than around room temperature is often sparse (and in some cases, noted in Table 1, rate data are non-existent between room temperature and approximately 1100 K). Because the assignment of error limits (or uncertainties) is subjective, no uncertainties are specifically given for temperatures other than 298 K; the reader can make reasonable judgements based on the data shown in the Arrhenius plots for the individual alkanes and cycloalkanes.

The use of n = 2 in the three-parameter expression $k = AT^n e^{-B/T}$ is justified by the good fits resulting from its use (especially for the smaller alkanes for which more temperature-dependent studies have been carried out) and by the observation that the literature values of n in the three-parameter expression from experimental studies of the reactions of OH radicals with $\geq C_2$ alkanes (see the Tables of rate data in the article) range from 1.05-3.09 (both of these being for ethane) with an average of 2.0. For methane, a value of n = 2.82 is used based on the literature data.

As noted by the reviewer, the article cites the site-specific rate constants for propane, n-butane and 2-methylpropane derived from kinetic studies of the fully, partially and non-deuterated alkanes. These rate data have been included in the development of empirical estimation methods for the overall and site-specific rate constants for the reactions of OH radicals with alkanes and other organic compounds for which the reactions proceed by H-atom abstraction (see, for example, Kwok and Atkinson, 1995). How accurate these estimated site-specific rate constants are for

ACPD

3, S1923–S1925, 2003

the larger alkanes still remains to be seen; product data suggest that they are not particularly accurate, especially for branched alkanes (see, for example, Atkinson et al., 1995; Aschmann et al., 2002).

References

Atkinson, R.., Kwok, E. S. C., Arey, J., Aschmann, S. M.: Reactions of alkoxy radicals in the atmosphere, Faraday Discuss., 100, 23-37, 1995.

Aschmann, S. M., Arey, J., Atkinson, R.: Products and mechanism of the reaction of OH radicals with 2,2,4-trimethylpentane in the presence of NO, Environ. Sci. Technol., 36, 625-632, 2002.

Kwok, E. S. C., Atkinson, R.: Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: an update, Atmos. Environ., 29, 1685-1695, 1995.

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3, S1923–S1925, 2003