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Atmospheric
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Discussions

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

Anonymous Referee #1

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General Comments

This is a useful piece of work, well worthy of publication.

The reactions of OH radicals with hydrocarbons are of great importance in both atmospheric and combustion chemistry and good quality kinetics data are essential to the successful modelling of such systems. This publication is, therefore, highly relevant. The literature survey is comprehensive, the data have been carefully and critically assessed, and the recommendations carry the authority of the author who has great experience in both the generation of the data and in critical evaluation.

There is some overlap with the work of the NASA and IUPAC Panels on evaluation of kinetic data for atmospheric modelling but the present survey covers a much wider range of alkanes, including deuterated species, and extends the evaluation to higher temperatures. The work is an extension of the author's previous work on the evaluation of data on the kinetics of atmospheric reactions, bringing the material on OH+alkane reactions up-to-date and, perhaps, putting a bit more emphasis on the higher temperature data.

I have some reservations (see later) but, in general, these do not amount to substantial criticisms of the work. I am sure that the recommendations will be widely used in atmospheric modelling.

Specific Issues

1. The work is set out clearly, but it is quite a long document, and I think it would benefit from some kind of index, perhaps combined with a summary table of the recommendations.

2. The author has chosen to limit rather strictly his recommendations to the temperature range over which reliable data are available. Very often the modeller will wish to use the material outside this range. There are examples where the author could have extended his recommendations to a more useful temperature regime without too much compromise of the quality of the recommendations. An example is the OH+CH_4 reaction where the recommended expression is limited to temperatures less than 12 K even though there are data available at higher temperatures. The recommended expression extrapolates reasonably well to these high temperature data. Even though the author feels, quite rightly, that the high temperature data are less reliable, I feel that he could have been of greater service to the modeller if he had extended the range of use of his recommended expression to take in the high temperature regime with, of course, higher error limits. This point applies mainly to the high temperature limits of the recommendations but there are also examples at the low temperature limits.

3. Error limits on values of k are given at 298 K but not at other temperatures. Error limits are also given for E/R (or the corresponding term in the extended Arrhenius expression). Quite apart from the fact that one is a subjective estimate and the other is a

statistically derived quantity, these together do not allow the error at other temperatures to be derived – they may not even tell the user whether the error is larger or smaller than that at 298 K. Some estimate of the error limits at the high and low temperature limits should be given – that is part of evaluation.

4. I would like to have in the introduction some justification of the choice of the T^2 dependence of the pre-exponential term in the extended Arrhenius expression. On the face of it there is no reason why the data should conform to such a temperature dependence particularly in the instances where abstractable-H atoms from different sites are available. I think it is a pity also that it has been used rather slavishly. I appreciate that the $AT^2\exp(B/T)$ often provides a good fit to the data, and its choice may be reasonable when the available data are so scattered that allowing the T^n to be a fitting parameter would lead to unreasonable values of n, but these apart, I can see no reason why the value of n arising naturally from a three parameter fitting should not be recommended. In many instances in this review such a fitting should be possible.

5. An important limitation of the data is that there are so few studies of branching ratios. However, a number of expressions for k for H-abstraction from different sites, derived by others, are quoted without comment from the author. Since this paper is about evaluation of the available data I feel that some comment is required, to endorse the findings (or not), to indicate their limitations, and perhaps indicate to what extent they can be extended to other compounds.

Minor points/typos etc.

P.2 , line 3 ...over ...

P198, line 8 ...at room...

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 4183, 2003.