Atmos. Chem. Phys. Discuss., 6, S961–S971, 2006
www.atmos-chem-phys-discuss.net/6/S961/2006/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evaluated kinetic and photochemical data for atmospheric chemistry: Volume III – reactions of inorganic halogens" *by* R. Atkinson et al.

J. Burkholder (Referee)

James.B.Burkholder@noaa.gov

Received and published: 24 May 2006

IUPAC evaluations, published over the years, have proven to be of the highest quality and are generally used as a reference by atmospheric modelers and laboratory scientists. The publication of the evaluation and data sheets in ACP in addition to the web site updates will further enhance the distribution of this valuable resource. Therefore, I highly recommend this evaluation for publication. I would also like to acknowledge the tremendous efforts made by the evaluation panel members in putting together such a useful research tool.

Due to the volume and scope of the evaluation I have focused this review on the pre-

sentation and have not thoroughly checked the entries of every data sheet. I have a few general comments, in order of appearance in the manuscript, that require attention followed by a list of typographical errors, wording changes and corrections.

First, the evaluation needs to have some general way to identify what reactions have been updated since the last evaluation. This would be of great help in identifying what reactions need to be updated in models and considered in laboratory applications without having to search through the entire document. This would make the evaluation an even more powerful tool and absolutely needs to be incorporated in the document.

There are several photochemical reactions that are conspicuous by their absence: FO, FO2, ClO, BrONO, and BrNO2 to name a few. I would recommend adding these molecules to the photochemical reactions list and evaluation.

Page 2293, line 7 “Thermodynamics Data summary” There is no summary included in this document!! I assume that this summary is available elsewhere. However, for this publication to be complete (self-contained) it needs to be reproduced in this document.

Comments:

General formatting: cross section is hyphenated in most cases but on many occasions it is not. Make the document consistent. (I would not hyphenate.)

General formatting: check that there is spacing before and after +- symbols and before “x” in number expressions

Data Sheets formatting: The page formatting in the final version needs to be checked to avoid pages that are nearly blank following the title reaction. For example see data sheet III.A1.6.

Data Sheets formatting: What is the standard notation for reaction thermochemistry parameters? Should there be a subscript “r”?

Data Sheets formatting: Replace the dot between kJ mol-1 with a space

ACPD
6, S961–S971, 2006

EGU

Data Sheets formatting: Remove unnecessary punctuation (periods) following preferred values and reliability values

Page 2282; The * footnote is not associated with a corresponding * with the authors names in the title

Page 2283, line 6: Give link to IUPAC website here, the first place it is mentioned.

Page 2283, line 9: Change “are” to “were”

Page 2283: “data base” to “database” (this needs to be changed in other places as well)

Page 2284: “photochemical reactions”? is there a better term than reactions

Page 2285: Top, “3 Table 1. SummaryĚ” Why is there a “3” here?

Page 2285: “inorganic reactions” shouldn’t it be “inorganic halogen reactions”

Page 2285: Change table headings “k298” to “k(298 K)” and “Temp. dependence of k” to “k(T)”

Page 2285: Shift “del(E/R)” one line up

Page 2292: Delete kinetic table headings from the photochemical section

Page 2292: “The cited uncertainty is an expanded uncertainty corresponding approximately to a 95% confidence limit.” What is an expanded uncertainty? It also sounds funny to refer to this as an approximate 95% confidence limit. This sentence needs to be re-worded.

Page 2296, line 9: Insert comma after “sections”

Page 2296, line 12: “Sect. 1.2” should be “Sect. 4.2”

Page 2298, line 14: Define what the subscript “c” on the equilibrium constant means.

Page 2299, line 14: The collision efficiency is introduced without adequate background

ACPD
6, S961–S971, 2006

EGU

material. It might be better to delete this and reference the Cobos and Troe (2003) paper for the details.

Page 2300, line 16: Give an example of a reaction in the evaluation in which the chaperon mechanism is important.

Page 2301, line 17: “Sect. 1.3” should be “Sect. 4.3”

Page 2303, line 24: delete “also”

Page 2304, lines13-16: Delete the sentence starting with “To convert”. This does not necessarily clarify how to convert units or why you would want to make such a conversion.

Page 2305, line 15: delete “come to”

Page 2305, lines 22-24: This is stated in the paragraph above and should be deleted.

Page 2306, line 3-4: “scarcity of apparently reliable data” this is a poor choice of words and should be re-written.

Data Sheets: Many of the comments contain statements such as “Discharge flow system” or “Pulsed laser photolysis” to describe the experimental measurements. However, the column “Technique/Comments” contains this same information and the introduction contains a long list of acronyms used in the evaluation. Editing the comments can minimize the redundancy. In particular, those comments that contain just a simple statement such as “Discharge flow system” should be changed. I have not highlighted all these cases but will leave that to the authors.

Data Sheets III.A1.2: The spacing in the rate constant values in the preferred values and reliability is missing. (This also occurs in other data sheets and needs to be checked globally).

Data Sheet III.A1.2: The recommended value is not very close to the gas collision frequency as stated in the comments.

ACPD

6, S961–S971, 2006

Data Sheet III.A1.3: Given the guidelines of the evaluation should the Wine et al. work be included in the comment section seeing that it is not in the table, not a new measurement, and not considered in the evaluation.

Data Sheet III.A1.4, line 6: Delete “of the literature data for this reaction”

Page 2320, line 15: Change “data-base” to “database”

Data Sheet III.A1.11, Page 2334, line 14: Delete “only two” Data Sheet III.A1.13, Page 2338, Lines 7: Change “monitored in absorption” to “monitored by absorption” (this phrase also needs to be changed in other comments)

Data Sheet III.A1.13, Page 2338, Lines 8: and “in presence” to “in the presence”

Data Sheets III.A1.13 and III.A1.15: Can you list possible reaction channels and add the thermochemistry to the data sheets

Data Sheet III.A2.16: It would be worth adding a comment describing the conditions and methods used in this measurement. For example, how was the HOCl or O atom concentration quantified?

Data Sheet III.A2.17: The comments are not in order with their appearance in the table

Data Sheet III.A2.17, page 2348,line 5: Delete “k”

Data Sheet III.A2.17, page 2348,line 8: Change to “in a slow flow reactor”

Data Sheet III.A2.17, page 2348,line 13: What are “other routes”

Data Sheet III.A2.17, page 2348,line 15: Delete “k”

Data Sheet III.A2.17, page 2348,line 16: Delete “k”

Page 2357, line 18: delete “still”

Page 2360, line 5: What does “data analysis difficulties” mean?

Data Sheet III.A2.22: Add high temperature range used in the Kumaran et al. study to

ACPD
6, S961–S971, 2006

the table with reference to comment (b)

Data Sheet III.A2.31, comment: If the agreement with the earlier study of Cox et al. 1987 is not good, is it reasonable to assume the temperature dependence from this study is OK.

Data Sheet III.A2.32, comment b: Is it appropriate to give the results for k at the different temperatures from the Toohey study?

Data Sheet III.A2.34: I would recommend that unpublished data not be referenced or used.

Data Sheet III.A2.37, page 2408, line 3: What is meant by “paid careful attention” ?

Data Sheet III.A2.17, page 2348,line 16: Delete “k”

Data Sheet III.A2.39: It is not clear to me that the results from the OD studies (Lipson et al., 1997) directly translate into the product branching ratios for the OH reaction. This may be addressed in their paper but some discussion is needed in the comments here. Also, line 12 should reference both Lipson et al. 1997 and 1999. The Tyndall et al. work in conjunction with the preferred value for the total rate coefficient also yields a branching ratio and should be considered in the comment.

Data Sheet III.A2.40: The recent paper by Gierczak et al. 2006 (Int. J. Chem. Kinet. 38(4), 234, 2006) should be included in the evaluation of this reaction.

Data Sheet III.A2.41, page 2420, line 9: Insert space “sole chlorine”

Data Sheet III.A2.44: Indent the second line of the Stimpfle et al. entry to clearly indicate that it is part of the rate coefficient expression given in the line above.

Data Sheet III.A2.44: Consider removing unpublished results from Laszlo et al.

Data Sheet III.A2.48, page 2441, Comment (a): “computer analysis” What does this mean? (This statement is used in a number of other comments.)

ACPD

6, S961–S971, 2006

Data Sheet III.A2.48: Biggs et al. used an absorption cross section for NO3 which has since been revised upward by about 30%. How does this affect their conclusions concerning the reaction branching ratio?

Data Sheet III.A2.51, line 14: Replace {} with ()

Data Sheet III.A2.54: Have the products of this reaction been identified? Are there other possible channels available

Data Sheet III.A3.58: Technique for Monks et al. study is given as DL-MS, DL is not defined should this be DF

Data Sheet III.A3.62, page 2480, line 11: Ninomiya et al. was included in the Arrhenius fit but the table does not indicate that a temperature dependence was reported in this study. Please clarify.

Data Sheet III.A3.64: There are no error limits given for the Toohey Arrhenius expression. Please add. Also, is it necessary to report the rate coefficient data from this study in the comment?

Data Sheet III.A3.66: Do you want to quote unpublished results here? It might be better not the quote a value at all. Data Sheet III.A3.67: The table should give the temperature range of the Sims et al. measurements as quoted in comment (c).

Data Sheet III.A3.67, page 2490, line 16: should this be “a un-weighted least-squares”

Data Sheet III.A3.69, page 2497, line 9: delete the second “from” on the line

Data Sheet III.A3.71: Are the reaction products BrOO + NO2 well established, could you get OBrO as a product?

Data Sheet III.A3.73: The study of Melluoki et al. 1994 (JGR, 99(D11), 22949- 22954) established a limit for channel (2) of $<$0.01% by studying the reverse reaction. This result should be included in the evaluation of the

ACPD
6, S961–S971, 2006

BrO + HO2 reaction. Data Sheet III.A3.74, page 2510, line 9: change “1000 mbar” to “1 bar”

Data Sheet III.A3.77: There is no mention of channel (5) in the evaluation. Should it be deleted?

Data Sheet III.A3.78, page 2528, line 10: delete comma

Data Sheet III.A3.78, page 2529, line 17: change “1000 mbar” to “1 bar”

Data Sheet III.A4.80, page 2536, line 9: change subscript 3 to superscript 3

Data Sheet III.A4.81: Add techniques to the table

Data Sheet III.A4.92: Add techniques to the table

Data Sheet III.A4.92: There is no mention of channel (5) in the evaluation.

Data Sheet III.A4.93: Add technique for Rowley et al.

Data Sheet III.A4.93, page 2573, line 21: change “1000 mbar” to “1 bar”

Data Sheet III.A4.93: There is no mention of channel (5) in the evaluation.

Data Sheet III.A4.94: Add techniques to the table

Data Sheet III.A4.94, page 2578, line 26: change “1000 mbar” to “1 bar”

Data Sheet III.A4.94, page 2580, line 15: change “1000 mbar” to “1 bar”

Data Sheet III.A4.95, page 2584, line 24: Should the IUPAC reference be updated to this evaluation?

Data Sheet III.A4.96, page 2588, line 20: Can the reference to the Blitz et al. work be updated and included in the evaluation. If not it should be deleted from the discussion.

Photolysis Data Sheets formatting: The photolysis data sheets do not all have the same layout. The first few do not contain an “Absorption cross section data” summary

ACPD
6, S961–S971, 2006

EGU

of the studies considered in the evaluation.

Photolysis Data Sheets formatting: It would be useful to add to the comments column in the “Absorption cross section data” summary the techniques used in the measurements in a similar fashion to the kinetics data sheets. Techniques could include acronyms for scanning spectrometer, diode array spectrometer, pulsed photolysis-transient absorption, cavity ring-down, and others.

Data Sheet III.A5.102, page 2603: The numbers given in the table are mixed up and are not presented in order going down the columns (looks like a problem with the page break).

Data Sheet III.A5.103, page 2608, line 6: The band peaks are referred to as a(0) to a(26) but are not labeled in the table given above.

Data Sheet III.A5.104: What are the recommended quantum yields?

Data Sheet III.A5.107, page 2634, line 10: insert space “values are”

Data Sheet III.A5.108, page 2638, line 1: “Because of the instability of ClONO,Ĕ” I don’t follow this logic. The photodissociation is not necessarily related to a molecules thermal stability. This statement needs to be changed.

Data Sheet III.A5.110, page 2634, line 16: Change “Broad band” to “Broadband”

Data Sheet III.A5.110, page 2635, line 5: What is the justification for a linear wavelength dependence to the quantum yield? Please explain why this formulation is included and where it comes from because this will influence photolysis quantum yields and calculated atmospheric ozone destruction.

Data Sheet III.A5.113: Studies other than Ingham et al. need to be included in the “Absorption cross section data” summary table.

Data Sheet III.A5.113: Cross section data at wavelengths less than 260 nm, the lower limit of the Ingham et al. study, from studies other than Ingham et al. needs to be

ACPD
6, S961–S971, 2006

included in the preferred values table.

Data Sheet III.A5.113, page 2645, lines 19-21: Results from photolysis rate calculations are presented here. This is nice information but I am not sure it belongs in the evaluation seeing that atmospheric photolysis rates in general are not reported for all molecules.

Data Sheet III.A5.115, page 2654, lines 5-8: What about analogy with OIO, the picture is not nearly as clear as to what the photolysis products and yields would be?

Data Sheet III.A5.116, page 2656, lines 9-10: This statement is WRONG! Corrections to the absorption spectrum were made only for Br2. A number of possible BrONO2 sample impurities were evaluated quantitatively and found to be negligible. I refer you to the paper for the details.

Data Sheet III.A5.117, page 2660, line 10: This link was re-directed when I tried it. Please check and update if needed.

Data Sheet III.A5.120, page 2674, line 2: I am not sure how to interpret “was tentatively attributed to”. Does this mean their spectrum is in error or not? With just two studies how do you tell which is correct Bauer et al. or Rowley et al.

Data Sheet III.A5.121, page 2678: The spacing in comment (c) looks funny.

Data Sheet III.A5.121, page 2679: The IO absorption cross section data given in the table is WRONG! The 4-0 band at ˜427 nm should be the spectrum maximum with a cross section of 3.5 x10(-17) cm2. See figure 2 in the Harwood paper for comparison.

Data Sheet III.5.123, page 2689: I would guess that the number of significant figures given for the cross section values in the table is too high.

Data Sheet III.5.123, page 2690, line 2: Mention where the values came from.

Data Sheet III.5.124, page 2693: I would guess that the number of significant figures given for the cross section values in the table is too too high.

ACPD
6, S961–S971, 2006

EGU

Data Sheet III.5.124, page 2694, line 2: Mention where the values came from even though there is only one source.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 2281, 2006.