Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-940-AC4, 2021

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VIII – gas phase reactions of organic species with four, or more, carbon atoms ($\geq C_4$)" *by* Abdelwahid Mellouki et al.

Abdelwahid Mellouki et al.

mellouki@cnrs-orleans.fr

Received and published: 8 February 2021

Referees #4 (Cornelius Zetzsch and Geert Moortgat): This current article is a supplement to the "Evaluated kinetic and photochemical data for atmospheric chemistry, Volume II; gasâĂŘphase reactions of organic species" (Atkinson et al., 2006). It updates existing data sheets, presents several new ones and continues to be a valuable tool for the scientific community. The kinetic and photochemical datasheets of the present work are (or are about to be) accessible in the internet (www.iupac.poleâĂŘether.fr). The manuscript is clearly publishable in ACP, where the readers may take the oppor-

tunity to add hints at errors and other work for consideration (further to corresponding with the lead author or any other member of the task group). The article starts with an introduction into the series with volumes on Ox, HOx, NOx, and SOx species organic species (the topic of the present work) inorganic halogens organic halogen species heterogeneous reactions on solid substrates heterogeneous reactions with liquid substrates and, in preparation, reactions of organic species with ozone and chemistry of Criegee intermediates It continues to present a guide to the datasheets with precise information on the equations of the functions employed and to the assignment of uncertainties in the recommendations of rate coefficients and Arrhenius parameters for room temperature and below. Moreover, the supplement shows Arrhenius diagrams for more than 40 molecules (how many alkanes, olefins and terpenoids, alcohols, aldehydes, acids, nitro compounds, aromatics?) and diagrams of UV absorption crossâĂŘ sections for 8 molecules. You may wish to list the Arrhenius diagrams with trivial names of the molecules on page 2, line 69 and might point out features of positive and negative temperature dependence (and convex and concave curvature), to be observed in the supplement.

General and specific comments and technical corrections:

P. 1, L. 25: The abstract might mention that the present work is a continuation of Volume II (Atkinson et al., 2006) with new (which molecules?) and updated data sheets for Appendix A2 (HO reactions), A3 (NO3 reactions) and A8 (photochemical processes). Reply: Done

P.1, l. 26: Have all of the data sheets of the present supplement been evaluated in 2019 or should the date be given individually for each data sheet or should the IUPAC website be consulted? Reply: The latest evaluation dates are now given in the datasheets

P. 3, line 73: gasâĂŘphase might be cancelled (see title) Reply: Done

P. 4: There are further abbreviations in the supplement, which could be listed, such as API, FEP, CEAS, IBBCEAS, ToF, EUPHORE reply: Abbreviations: API, FEP, CEAS,

IBBCEAS, ToF added

P. 9, l. 285: Are there appropriate, obvious examples for combination reactions without a barrier? Reply: In this general section we would like to maintain consistency with previous IUPAC publications and prefer not to give examples.

P. 12, l. 386: In which cases is H2O a particularly efficient third body? Reply: In this general section we would like to maintain consistency with previous IUPAC publications and prefer not to give examples.

P.12, l. 398: Photochemical transitions or processes? The data sheets comprise cases, where available UV spectra have not been discussed down to 170 nm, where UV spectra for, e.g., 2âĂŘnitrophenol are available (http://satellite.mpic.de/spectral_atlas). Reply: Taken into account: - Processes is used and 170 nm replaced by 185 nm

P. 14, l. 460: “Unfortunately” or better: “On the other hand” or “Moreover” (?). Reply: “However” is used

This situation stimulates further investigation with improved techniques, wider ranges of concentration, total pressure and temperature, or detailed consideration of the tail of nonâĂŘexponential decays as biexponential, triexponential, multiexponential or mixed with second order components

P. 14, l. 463âĂŘ466: Some more reasons for such differences of more than a factor of two could be listed here, such as insufficient purity of compounds, unknown/unexpected impurities, wall adsorption and decomposition, insufficient time resolution for the initial elementary step, opposing and parallel reactions or unexpected decomposition products from the primary product. Reply: The following has been added: “The differences between various measurements could be due to multiple reasons, such as insufficient purity of compounds, unknown/unexpected impurities, wall adsorption and decomposition, insufficient time resolution for the initial elementary step, opposing and parallel reactions or unexpected decomposition products from the primary

product.”

P. 15, line 473: “scarcity of reliable data” => could you delete “reliable” (?) Reply: Done

P. 15, line 483: IUPAC. For the => IUPAC for the Reply: Done

P. 16. line 524: “J. Phys. Chem. Ref. Data” occurs twice Reply: The second has been deleted

P. 17, line 550: One might expect the series of evaluations by Atkinson (monographs) and by Calvert et al., most of which are mentioned in the supplement in several datasheets, to be cited here as well. Reply: Our introductory text gives an overview of the work of the IUPAC panel but does attempt to provide a comprehensive listing of previous evaluations / databases of kinetic data.

P. 19âĂŘ22: Overall or overall? Reply: Done

P. 22: Table 1 should end with the NO3 reactions and the footnote, and the photochemical reactions should be a separate Table 2 (with different entries, such as absorption crossâĂŘsections and quantum yields?). Reply: The photochemical data is not parameterised in a systematic manner that can be easily tabulated in a short form for all of the datasheets. Therefore, we have chosen to simply list the processes covered and name the datasheet in which the details about the absorption spectrum and the quantum yields can be found.

Supplement General remarks on the text

It occurs in several places of the supplement (unlike the main manuscript) that the list of authors in the references does not end with a colon before the journal follows (in the photolysis section mainly). Reply: Corrected

Exponents and their numerals should not appear in separate lines. Reply: Corrected

The dates of final evaluation (and recommendation) should be mentioned in the heading of every data sheet, like those available on the website.

Reply: Done

Unlisted authors (et al.), isomers cis, trans, HâĂŘ, nâĂŘ and iâĂŘ should be marked by italic fonts in the whole text, in the tables and in the comments. isomers cis, trans, HâĂŘ, nâĂŘ and iâĂŘare in italic now (al. not modified) The date of the IUPAC recommendations (IUPAC and year instead of Arrhenius fit (or biexponential fit on page 212) should appear in the figures Reply: For anyone interested, information concerning the date of the IUPAC evaluation and the last change in preferred values can be readily accessed via the website for any particular datasheet.

The use of upper and lower case letters in headings, footnotes and figure captions is inconsistent. Reply: Corrected

Pages 1âĂŘ3 Some simple structures of aliphatics are missing, and trivial names of several molecules could be added as explanation in brackets, even for catechol. Reply: Chemical names are given in the table. The names and structures are given in datasheets

Tables on Pages 5 (nâĂŘbutane), 141 (benzene), 147 (toluene): Recent work exists on relative rate constants for 17 hydrocarbons, including nâĂŘbutane, benzene and toluene. These have been investigated at 248 and 288 K in a smog chamber by Han et al. (L. Han, F. Siekmann, C. Zetzsch: Atmosphere 9, 320, 2018, doi:10.3390/atmos9080320) in reasonable agreement with the IUPAC recommendations. Reply: Thanks to the reviewer, the above data have been added.

Page 141, Line 4110: => pressure. The nonâĂŘexponential decays were shown to be biexponential by Wahner and Zetzsch (1983), Knispel et al. (1990), and Bohn and Zetzsch (1999), according to the analytical solution of the differential equation system, where the backâĂŘdecomposition of the HOâĂŘbenzene adduct, leads to an equilibration of OH with the adduct, considering the abstraction channel as irreversible loss process of OH and the adduct. Reply: The suggestion was added to the end of comment (f): (f) Rate coefficients were measured over the pressure ranges 67-173

mbar (50-130 Torr) of Ar diluent (Wahner and Zetzsch, 1983) and 33-666 mbar (25-500 Torr) of He diluent (Rinke and Zetzsch, 1984), with a slight decrease in rate coefficient being observed below 133 mbar (100 Torr) pressure in both cases. The cited rate coefficients are at 133 mbar pressure. “The nonâĂŘexponential decays were shown to be biexponential by Wahner and Zetzsch (1983), Knispel et al. (1990), and Bohn and Zetzsch (1999), according to the analytical solution of the differential equation system, where the backâĂŘdecomposition of the HOâĂŘbenzene adduct, leads to an equilibration of OH with the adduct, considering the abstraction channel as irreversible loss process of OH and the adduct.”

Figures Unlisted authors (et al., sometimes those who spent their time performing the experiments or improving the equipment) are missing in several figures (especially the NO3 section), in some instances the second author as well. Reply: The present labelling system enables the responsible authors (listed in full in the references) to be identified unambiguously and avoids cluttering the Figures with too much information. All authors are listed correctly in the reference list, that is fine.

Not in all cases are the rate coefficients and Arrhenius expressions derived by other authors listed in the tables and shown in the graphs (this would help the reader even if no IUPAC recommendation is made for a single study of the temperature dependence). This holds even more so if an expression derived by other authors is adopted by IUPAC (e.g. nâĂŘbutane, adopted from Donahue and Clarke, 2004). Reply: Adding all reported Arrhenius expressions to the Figures would result (in many cases) in an unreadable graph and we prefer not to do this. Where available, we have listed the reported Arrhenius expressions to the tables in each data-sheet.

P. 8 (nâĂŘButane): correct Clark into Clarke, add tick marks or gridlines of the logarithmic scale. Gridlines might be added to all figures Reply: Clark corrected into Clarke. No change in the Figures made

P. 17 (Isoprene) The reaction HO + Isoprene does not appear in the figure as a label.

In the same fashion, labels with the reactions are missing on pages 22, 28, 79, 118, 122, 125, 128, 130, 132, 215, 217, 224, 226, 231, 233, 235, 237. Reply: Done for all

Delete black boxes around the reaction labels on pages 83, 86 and 197 Reply: Done for all

Except for a few aromatics, the abstraction channel has not been shown in the Arrhenius diagrams. Equilibration of OH and NO3 with the adduct may cause the negative activation energy for olefinic compounds and a concave curvature at high temperatures. Have available highâĂŘtemperature data or nonâĂŘexponential decays at intermediate temperatures been considered in all cases? Reply: In the Figures, we plot the overall rate constant. The (temperature dependent) fractional contribution of the abstraction and addition channels is parameterised in the table of preferred valued.

Technical corrections

Line 2853: at al. => et al. Reply: Not changed Line 2969: at al. => et al. Reply: Not changed Line 3235: at al. => et al. Reply: Not changed Lines 3450 and 6418: The asterisk might be explained by a footnote, or one might ask the authors for the correct temperature Reply: A footnote was added under the tables *) the experimental temperature was "room temperature" which we list as 298K. Line 4095: nonâĂŘexponential => biexponential: Done Line 4117: nonâĂŘexponential => biexponential: Done Line 4194: nonâĂŘexponential => biexponential: Done Line 4290: nonâĂŘexponential => biexponential: Done Line 4405: nonâĂŘexponential => biexponential: Done Line 4211: Somerlade => Sommerlade: Done Line 4789: nonâĂŘexponential => biexponential: Done Line 5656: to appear => add year of appearance (2011): Done

The following suggestions have been taken care of: Line 5834: => over 2âĂŘmethylpropene Line 5838: => over 2âĂŘmethylpropene Line 5840: => of 2âĂŘmethylpropene Line 6153: => Bunsenges. Lines 6186, 6286, 6525, 6600, 6763, 6836, 6968: NO3. So that.... => NO3, so that Line 6436: 1 bar Lines 6542, 6781, 6861, 6922: accurate => absolute Line 6746: BunsenâĂŘGes. => Bunsenges. Line 6876: Bun-

senâĂŘGes. => Bunsenges. Line 6879: cancel VOC55 Line 7030: 8âĂŘmethylene.. Line 7254: 7âĂŘtetra Line 7290: aâĂŘdimethyl Line 7329: aâĂŘhexa.. Line 7463: was obtained. Line 7533: agreement, and => agreement and (?) Line 7566: RRGC => RRâĂŘGC Line 7617: butene. Line 7622: 5âĂŘmethyl... Line 7679: butene.

Photochemistry section

General comments

1 Selection criteria In this supplement of Volume II (Atkinson et al., 2006), 8 organic species with four, or more, carbon atoms ($\geq$ C4) were evaluated. What are the criteria of the selection of those eight organic species? More photolysis studies of organic species ($\geq$ C4) have been published in the literature, which could have been evaluated in this supplement. Examples are: nâĂŘbutanal and nâĂŘpentanal (Tadic et al., 2001a), nâĂŘhexanal (Tadic et al., 2001b), nâĂŘheptanal (Tadic et al., 2002), nâĂŘoctanal (Tadic et al., 2011), transâĂŘcrotonaldehyde (Magneron et al., 2002) and methyl ethyl ketone (Nádasdi et al., 2010) References Magneron, I., Thévenet, R., Mellouki, A., Le Bras, G., Moortgat, G. K. and Wirtz, K.: J. Phys., Chem., A, 106, 2526 (2002). Nádasdi, R., Zügner, G. L., Farkas, M., Dóbé, S., Maeda, S. and Morokuma, K.: Chem. Phys. Chem., 11, 3883 (2010). Tadic, J., Juranic, I. and Moortgat, G. K.: J. Photochem. Photobiol. A: Chem., 143, 169 (2001a). Tadic, J. M., Juranic, I. and Moortgat, G. K.: Molecules, 6, 287 (2001b). Tadic, J. M., Juranic, I. O. and Moortgat, G. K.: J. Chem. Soc., Perkin Trans., 2, 135 (2002).

Reply: A criterion that we generally use is that the oxygenate is a product of a hydrocarbon or other species in the evaluation. A large number of species has not been evaluated so far. This will be done in the future. However, we have updated the datasheet for butanone (P8) and added it to the present volume.

2 Presentation a) In the Summary page (p 271, line 8010) one product channel is given, which is not correct. One ought to replace this by "products", as is shown in the datasheets, or add the other product channels Reply: Corrected

b) The head texts of the current datasheets are different from those presented in Volume II (Atkinson et al., 2006). The text that appeared on the website (iupac.poleâĂŘether.fr) contains additional information, such as the update date Reply: Head texts of the datasheets completed with the dates

c) In the title molecule, it would be advisable to add the trivial name d) The presentation section starts with “Primary photochemical transitions” However, in older datasheets of Volume IV (Atkinson et al., 2008), this title was named “Primary photochemical processes”. Would this title be more appropriate? e) In all photochemical datasheets, the substances appear above the figure Reply: The substances are now in the Figures boxes

3 Technical corrections A) Throughout the text in Volumes II and VIII, the references are not presented uniformly. It is advisable to use the same citation style throughout the manuscript, including the supplement The references are presented uniformly B) Units. The text should use for the cross-section units cm2 molecule-1 and not cm2molecule-1 nor cm2/molecule Reply: cm2 molecule-1 is used Additional figures of the spectra on a logarithmic scale (or a reference to the Spectral Atlas, where these are an option) might be useful. Term symbols of the transitions (absorption bands displayed in the figures) and rough estimates of the oscillator strengths would be useful and a key to the photolytic processes. Reply: Our emphasis is on cross-sections, and quantum yields (which are needed to evaluate the lifetime and role of any trace gas in the atmosphere) and not spectroscopic details of the excited states involved.

C) Individual remarks P23 : all suggestions taken into account Line 8022 add trivial name: biacetyl Line 8027 align reaction products Line 8063 correct p = ∞ into p $\rightarrow \infty$ Line 8071 remove one comma: Horowitz et al. (2001), which are. . .. Line 8092 correct: Barnes, I. and Becker K. H., Line 8094 correct: Calvert, J. G. and Pitts Jr., J. N., Line 8098 correct: Ravishankara, A. R. and Burkholder, J. B., Line 8104 correct: Absorption spectrum of biacetyl

P24 all suggestions taken into account Line 8111 add trivial name: iâĂŘbutyraldehyde Line 8114 align reaction products Line 8130 correct: with a resolution Line 8135 remove comma: . . . determined from measurements. . . Line 8153/54 rewrite: . . .except for very slightly at 330.5 nm . »» . . ..except at 330.5 nm, where a minimal pressure dependence was observed. Line 8174 replace:. . . better than 4 %... by . . . smaller than 4% Line 8197 correct: . . .Francisco, J. S.: J. Phys. Chem. A, ... 2002. Line 8200 correct: Calvert, J. G. and Pitts Jr., J. N., Line 8206 correct: Absorption spectrum of iâĂŘbutyraldehyde

P26 all suggestions taken into account Line 8213 add trivial name. Note: two different names appear in the text: butenendial and buteneâĂŘ2âĂŘdial It is assumed that butane-2-dial is correct, and should be corrected throughout the text. Line 8213 move arrow, and align product channel numbers Line 8219 correct reference: Hufford et al., 1952. Line 8222 the transitions “cisâĂŘ/trans & trans/âĂŘcis” should be in italics font Line 8226 the Comments a, b, c, d, and e, are erroneously labeled a, b, c, c,and d Lines 8230, 8232, 8240 correct units to: cm2 molecule-1 Line 8232 move right bracket: purified (crystalline) fumaric dialdehyde Lines 8232 and 8239 correct: crossâĂŘsections (not cross sections) Line 8242 insert commas: at 193 nm, HCO produced by the Cl + HCHO reaction, was. . . Line 8243 delete “ in” Line 8247 correct: “was” into “were” Line 8253 correct: assigned Lines 8255 and 8282: add year (1994) of reference Line 8257 change temperature to 298 K Line 8271 correct Fig 1 to Fig. 1 Line 8278 insert comma after . . .limits »>. . . limits, Line 8287 correct: . . .. Barnes, I., Becker, K. H. and Wiesen, P., Environ. Sci. Technol. Line 8289 correct: . . .Chem. Phys. Lett. Line 8242 enter space between first names of authors Line 8305 correct: Absorption spectrum. . .

P27 all suggestions taken into account Line 8311 Note: three different names appear in the text: 4âĂŘoxoâĂŘpentâĂŘ2âĂŘenal , 4âĂŘoxoâĂŘ2âĂŘpentenal and 4âĂŘoxoâĂŘpentenâĂŘ2âĂŘdial (see figure caption) Which is correct?, This should be corrected throughout the text. Line 8313 align product channels Line 8322 the transitions “cisâĂŘtrans & transâĂŘcis” should be in italics Line 8328

and further throughout this comment section: correct crossâĂŘsection (not cross section) Lines 8352 and 8354 correct: 5âĂŘmethylâĂŘ3HâĂŘfuranâĂŘ2âĂŘone, not 5âĂŘMethylâĂŘ3HâĂŘfuranâĂŘ2âĂŘone Line 8358 add year (1994) of reference Line 8370 change temperature to 298 K Line 8378 correct: ... study of the gasâĂŘphase... Line 8383 enter space: 193 nm Line 8395 insert comma after: However,... Line 8397 correct Bierbach et al. (1994) Line 8401 add year (1994) of reference Line 8411 correct figure caption: .. spectrum of [enter correct name]

P28 Line 8421: Absorption crossâĂŘsection data and quantum yields of M. Sangwan and L. Zhu ("Absorption cross sections of 2âĂŘnitrophenol in the 295âĂŘ400 nm region and photolysis of 2âĂŘnitrophenol at 308 and 351 nm," J. Phys. Chem. A 120, 9958âĂŘ9967, 2016) are not discussed. Absorption crossâĂŘsection data of S. A. Shama ("Vacuum ultraviolet absorption spectra of organic compounds in gaseous and liquid state," PhD Thesis, Faculty of Science (Benha) Zagazig University, Egypt, 1991, http://library.mans.edu.eg/eulc_v5/Libraries/Thesis/BrowseThesisPages.aspx?fn=PublicDrav of monoâĂŘ and disubstituted aromatics above 170 nm are missing, see MPIC Spectral Atlas. Reply: The data from M. Sangwan and L. Zhu have been added to the datasheet P28. In addition P31 and P32 have been updated. However, we do not use non-peer reviewed sources Line 8435 correct: Chen et al. (2011) Line 8441 delete in title “for 2âĂŘnitrophenol” Line 8459 correct: e.g. Line 8461 rewrite: The quantum yields are based on photolysis rates observed under defined conditions Not: the quantum yield based on photolysis rates observed by under defined conditions Line 8469 correct ..... Peter, P. and Benter Line 8471 Bardini, P. Line 8472 correct: Wenger, J. C. and Venables, D. S., Line 8655 Bardini, P.

P30 all suggestions taken into account Line 8485 add trivial name: benzaldehyde Line 8494 align references in table Line 8500 and further throughout this comment section: correct crossâĂŘsections (not cross sections) Line 8509 correct: ..investigated at wavelengths Line 8520 units are missing: cm2 moleculeâĂŘ1 Line 8525 rewrite: ... determined by the “factor analysis method”, where the spectrum obtained is refined

and... Line 8527 correct: complex Line 8529 sentence is incomplete: give wavelength range Lines 8553 and 8554: correct units: cm2 moleculeâĂŘ1 Line 8557 and 8558: rewrite: ... and those of Zhu and Cronin (2000), which are significantly lower than other measurements, except at 318 nm where they are slightly higher. Line 8561 correct: Chen et al.... not ... at al. Line 8563 rewrite sentence: ...and an offset in their absorption at λ > 380 nm, probably resulting from a baseline shift or noise. Line 8565 correct: Thiault et al. (2004) blue shifted by 4 nm... Line 8570 remove “at” Line 8571 correct: may be unrepresentative.... (delete ”in”) Line 8572 insert comma after “Nevertheless” Lines 8575 to 8589: enter space between first names of authors Line 8584 correct: Nozière, B., further put first names behind authors

P31 all suggestions taken into account Lines 8612 and 8617 correct: crossâĂŘsections (not cross sections) Lines 8621 correct 3âĂŘmethylâĂŘ2âĂŘnitrophenol Line 8628 delete “for 3âĂŘmethylâĂŘ2âĂŘnitrophenol” Line 8637 correct crossâĂŘsections (not cross sections) Lines 8640 and 8646 correct 3âĂŘmethylâĂŘ2âĂŘnitrophenol Line 8641 correct : cm2 moleculeâĂŘ1 Line 8644 correct: Bejan et al. (2006) Line 8645 correct reference into: Bejan et al. (2007) Line 8647 correct redâĂŘshifted Line 8651 correct ....Kleffmann, J., Lines 8653 and 8656: remove comma before “and” Line 8656 enter space between first names of authors

P32 all suggestions taken into account Lines 8678 and 8683 correct: crossâĂŘsections (not cross sections) Line 8693 delete “for 4âĂŘmethylâĂŘ2âĂŘnitrophenol” Line 8702 correct: crossâĂŘsections (not cross sections) Line 8707 correct : cm2 moleculeâĂŘ1 Line 8708 correct : acetonitrile (not acetonitryl) Line 8711 correct: Bejan et al. (2007) Line 8716 correct ....Kleffmann, J., Lines 8718 and 8621 remove comma before “and”

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-940, 2020.