## Referees Cornelius Zetzsch and Geert Moortgat

IUPAC data evaluation. Review of Manuscript acp-2020-940

This current article is a supplement to the "Evaluated kinetic and photochemical data for atmospheric chemistry, Volume II; gas-phase 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.pole-ether.fr). The manuscript is clearly publishable in ACP, where the readers may take the opportunity 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

$O_x$, $HO_x$, $NO_x$, and $SO_x$ 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 cross-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 ($NO_3$ reactions) and A8 (photochemical processes).

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?

P. 3, line 73: gas-phase might be cancelled (see title)

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

P. 9, l. 285: Are there appropriate, obvious examples for combination reactions without a barrier?

P. 12, l. 386: In which cases is $H_2O$ a particularly efficient third body?

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., 2-nitrophenol are available (http://satellite.mpic.de/spectral_atlas).

P. 14, l. 460: “Unfortunately” or better: “On the other hand” or “Moreover” (?). This situation stimulates further investigation with improved techniques, wider ranges of concentration, total pressure and temperature, or detailed consideration of the tail of non-exponential decays as biexponential, triexponential, multiexponential or mixed with second order components

P. 14, l. 463-466: 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

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

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

P. 16. line 524: “J. Phys. Chem. Ref. Data” occurs twice

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.

P. 19-22: Overall or overall?

P. 22: Table 1 should end with the $NO_3$ reactions and the footnote, and the photochemical reactions should be a separate Table 2 (with different entries, such as absorption cross-sections and quantum yields?).

## 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).

Exponents and their numerals should not appear in separate lines.

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

Unlisted authors (*et al.*), isomers *cis*, *trans, H-, n-* and *i-* should be marked by italic fonts in the whole text, in the tables and in the comments.

The date of the IUPAC recommendations (IUPAC and year instead of Arrhenius fit (or biexponential fit on page 212) should appear in the figures

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

Pages 1-3 Some simple structures of aliphatics are missing, and trivial names of several molecules could be added as explanation in brackets, even for catechol.

Tables on Pages 5 (*n*-butane), 141 (benzene), 147 (toluene): Recent work exists on relative rate constants for 17 hydrocarbons, including *n*-butane, 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.

Page 141, Line 4110: => pressure. The non-exponential 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 back-decomposition of the HO-benzene 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 $NO_3$ section), in some instances the second author as well.

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. *n*-butane, adopted from Donahue and Clarke, 2004).

P. 8 (*n*-Butane): correct Clark into Clarke, add tick marks or gridlines of the logarithmic scale. Gridlines might be added to all figures

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.

Delete black boxes around the reaction labels on pages 83, 86 and 197

Except for a few aromatics, the abstraction channel has not been shown in the Arrhenius diagrams. Equilibration of OH and $NO_3$ with the adduct may cause the negative activation energy for olefinic compounds and a concave curvature at high temperatures. Have available high-temperature data or non-exponential decays at intermediate temperatures been considered in all cases?

## Technical corrections

Line 2853: at al. => *et al.*

Line 2969: at al. => *et al.*

Line 3235: at al. => *et al.*

Lines 3450 and 6418: The asterisk might be explained by a footnote, or one might ask the authors for the correct temperature

Line 4095: non-exponential => biexponential

Line 4117: non-exponential => biexponential

Line 4194: non-exponential => biexponential

Line 4290: non-exponential => biexponential

Line 4405: non-exponential => biexponential

Line 4211: Somerlade => Sommerlade

Line 4789: non-exponential => biexponential

Line 5656: to appear => add year of appearance (2011)

Line 5834: => over 2-methylpropene

Line 5838: => over 2-methylpropene

Line 5840: => of 2-methylpropene

Line 6153: => Bunsenges.

Lines 6186, 6286, 6525, 6600, 6763, 6836, 6968: $NO_3$. So that…. => $NO_3$, so that

Line 6436: 1 bar

Lines 6542, 6781, 6861, 6922: accurate => absolute

Line 6746: Bunsen-Ges. => Bunsenges.

Line 6876: Bunsen-Ges. => Bunsenges.

Line 6879: cancel VOC55

Line 7030: 8-methylene..

Line 7254: 7-tetra

Line 7290: a-dimethyl

Line 7329: a-hexa..

Line 7463: was obtained.

Line 7533: agreement, and => agreement and (?)

Line 7566: RRGC => RR-GC

Line 7617: butene.

Line 7622: 5-methyl…

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 (≥ $C_4$) were evaluated.

What are the criteria of the selection of those eight organic species? More photolysis studies of organic species (≥ $C_4$) have been published in the literature, which could have been evaluated in this supplement.

Examples are: *n*-butanal and *n*-pentanal (Tadic *et al.*, 2001a), *n*-hexanal (Tadic *et al.*, 2001b), *n*-heptanal (Tadic *et al.*, 2002), *n*-octanal (Tadic *et al.*, 2011), *trans*-crotonaldehyde (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).

Tadic, J. M., Lai Xu, Houk, K. N. and Moortgat, G. K.: J. Org. Chem., 76, 1614 (2011).

## 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
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.pole-ether.fr) contains additional information, such as the update date
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

## 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

B) Units.

The text should use for the cross-section units

$cm^2$ $molecule^{-1}$ and not $cm^2 molecule^{-1}$ nor $cm^2/molecule$

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.

## C) Individual remarks

### P23

Line 8022 add trivial name: biacetyl

Line 8027 align reaction products

Line 8063 correct $p = \infty$ 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

Line 8111 add trivial name: *i*-butyraldehyde

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 *i*-butyraldehyde

### P26

Line 8213 add trivial name.

Note: two different names appear in the text:

butenendial and butene-2-dial

It is assumed that butene-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 "*cis-/trans & trans/-cis*" 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: $cm^2$ $molecule^{-1}$

Line 8232 move right bracket: purified (crystalline) fumaric dialdehyde

Lines 8232 and 8239 correct: cross-sections (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

Line 8311 Note: three different names appear in the text:

4-oxo-pent-2-enal , 4-oxo-2-pentenal and

4-oxo-penten-2-dial (see figure caption)

Which is correct?, This should be corrected throughout the text.

Line 8313 align product channels

Line 8322 the transitions "*cis-trans & trans-cis*" should be *in italics*

Line 8328 and further throughout this comment section:
correct cross-section (not cross section)

Lines 8352 and 8354 correct: 5-methyl-3*H*-furan-2-one, not 5-Methyl-3H-furan-2-one

Line 8358 add year (1994) of reference

Line 8370 change temperature to *298* K

Line 8378 correct: … study of *the* gas-phase…

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 cross-section data and quantum yields of M. Sangwan and L. Zhu ("Absorption cross sections of 2-nitrophenol in the 295-400 nm region and photolysis of 2-nitrophenol at 308 and 351 nm," J. Phys. Chem. A 120, 9958-9967, 2016) are not discussed.

Absorption cross-section 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=PublicDrawThesis&BibID=9666196) of mono- and disubstituted aromatics above 170 nm are missing, see MPIC Spectral Atlas.

Line 8435 correct: Chen et al. (2011)

Line 8441 delete in title "for 2-nitrophenol"

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

Line 8485 add trivial name: benzaldehyde

Line 8494 align references in table

Line 8500 and further throughout this comment section:
correct cross-sections (not cross sections)

Line 8509 correct: ..investigated *at* wavelengths

Line 8520 units are missing: $cm^2$ $molecule^{-1}$

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: $cm^2$ $molecule^{-1}$

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 $\lambda > 380$ 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

Lines 8612 and 8617 correct: cross-sections (not cross sections)

Lines 8621 correct 3-*methyl*-2-nitrophenol

Line 8628 delete "for 3-methyl-2-nitrophenol"

Line 8637 correct cross-sections (not cross sections)

Lines 8640 and 8646 correct 3-*methyl*-2-nitrophenol

Line 8641 correct : $cm^2$ $molecule^{-1}$

Line 8644 correct: Bejan et al. (2006)

Line 8645 correct reference into: Bejan et al. (2007)

Line 8647 correct red-shifted

Line 8651 correct ….Kleffmann, J.,

Lines 8653 and 8656: remove comma before “and”

Line 8656 enter space between first names of authors

P32

Lines 8678 and 8683 correct: cross-sections (not cross sections)

Line 8693 delete “for 4-methyl-2-nitrophenol”

Line 8702 correct: cross-sections (not cross sections)

Line 8707 correct : $cm^2$ $molecule^{-1}$

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”