This manuscript represents a considerable progress in the structure – activity relations for reactions of OH with monocyclic aromatic compounds. It deals with a highly relevant class of aromatics for atmospheric chemistry, the hydroxy-nitrated phenols, and I recommend its publication in ACP.

The electron delivering lone-pair substituents (hydroxyl) interact with an electron withdrawing substituent (nitro) via the highly conductive aromatic π system and (even more) directly via H bonds to the nitro group. The H bond appears to increase the electron withdrawing capability of the nitro group enormously, resulting in a lower rate constant of electrophilic addition. A most striking example is the extremely low reactivity of 4-methyl- 5-nitrocatechol, where the effect of the electron-delivering methyl group is completely overrun by this interaction (even increasing the effect) and leads to an even lower reactivity than 4-nitrocatechol. Similar effects of the nitro group have been observed by the authors for the nitrophenols and can be expected for anilines and thiophenes (and possibly heterocyclic and polycyclic and multifunctional compounds), which occur as metabolites and can deliver electrons via the π system and an H atom to form an H bond to the vicinal nitro group.

The same interaction shows up convincingly in the gas-phase IR spectra, where the the H bond between the vicinal OH groups appears as broadened peak around 3100 wavenumbers for catechol and shifts to almost 3400 wavenumbers for 4-methyl- 5-nitrocatechol. I would like to suggest that these most interesting IR spectra are added to the title: “Investigations on the gas-phase photolysis, IR spectra and OH radical kinetics of nitrocatechols: Implications of intramolecular interactions on their atmospheric behavior” and that the outcome should appear in the abstract (see below) and be discussed in a little more detail.

The determination of the rate constants with two different reference compounds and the photolysis constants for two wavelengths (an illustration of these data is missing) has excellent quality, and the authors might wish to add the values of the wall reactions of figs. 1-4 to the figure captions (or to table 2). The abstract should include the photolysis of all studied compounds by mentioning the photolytic lifetimes and the upper limits of 28 h for the atmosphere instead of the photolysis constants. It is not clear from the heading of the right column in table 2 that the lifetime refers to the atmosphere (do not mention the 365 nm here but explain that this has been calculated on the basis of NO_2 photolysis in the chamber). Are UV spectra of the compounds available to give an estimate of quantum yields at the wavelengths of 254 and 365 nm?

Have any products from the reaction with OH or of photolysis been observed and identified from their IR spectra?

Considering fig. 5, additional figures of the gas-phase IR spectra of the nitrophenols of table 3 (and possibly the triols) are desirable to demonstrate if the H bonds show up and obey similar systematics (and if available). Surprisingly, you do not discuss the H bond and its shift to higher wavenumbers in the nitrated catechols, where you might indicate the shifts by arrows from the relevant peaks of 4MCAT via 5M3NCAT to 4M5NCAT and from CAT via 3NCAT to 4NCAT.

It would be nice to add a table with the wavenumbers (and widths) of the bands assigned to OH and O…H bonds and to discuss these and their shifts, the removal of the doublet and shape in terms of bond strength and loss of symmetry. The position of the OH stretching vibration is also slightly shifted and may be taken as a measure of the bond energy and portion of the abstraction channel. This may add value to the mesomeric/electromeric effects discussed in figure 6. In fact, the description of the addition of OH to monosubstituted monocyclic aromatics by electrophilic addition in the gas phase became accessible in 1980 and 1981 by determining the rate constants for OH + biphenyl, chlorobenzene, benzonitrile and nitrobenzene by research students who enabled us to determine the reaction constant for gas-phase addition of OH. Together with the rate constants for aniline and phenol determined by Rinke and Wahner this led to the regression log (k/cm^3s^{-1})= -11.7 – 1.41 σ^+ for the available literature data (excluding benzaldehyde, where abstraction was known to predominate) (Zetzsch, 1982, see below). The extension to disubstituted and polysubstituted monocyclic aromatics then included our own data for *o*- and *m*- dichlorobenzene and 1,2,4-trichlorobenzene and various mono- and polysubstituted benzenes from literature and led to the regression log (k/cm^3s^{-1})= -11.6 – 1.39 Σ σ^+. That regression, updated, adopted and properly cited by Kwok and Atkinson (1995), represented the available data within a factor of two and was enabled by the careful selection of the Hammett constants for electrophilic substitution by Brown and Okamoto (1958) from a large number of kinetic experiments in aqueous solution: Solvolysis of *t*-cumylchlorides, bromination, chlorination and nitration of aromatic derivatives, protonolysis of $ArylSiMe_3$, ionization of $Aryl_2CHOH$) and IR spectra of acetophenones and by the four "rules" in the conference abstract below. Brown and Okamoto pointed out that this database became extremely consistent if their σ^+ values were used rather than the "thermodynamic" σ values from equilibria.

It would be most interesting to evaluate the impact of the H bonds on the sum of the Hammett constants for electrophilic addition according to Brown and Okamoto and to propose revised constants for such combinations of lone-pair substituents with the nitro substituent (if such a consideration is reasonable at all). The very impressive last column of Table 3 then deserves a better resolution than only one digit, and you might wish to extend the data in Table 3 and their discussion to polycyclic aromatics, such as nitronaphthalenes, attempting to estimate/predict the OH-reactivity of nitronaphthols.

The SAR predictions of Table 4, adopting the procedures of Jenkin et al., adjusting the parameters to the experimental data, appear to underpredict the phenols and overpredict the catechols (4M5NCAT remains to be an unexplained extreme case). The different success of the SAR methods needs an additional figure to illustrate this limitation on the basis of the constants for electrophilic addition (and/or those of Jenkin et al.). Additional experimental and theoretical work on this topic is highly encouraged.

Technical corrections, minor questions and suggestions:

I feel that an alphabetical order of the references in the text is more justified than a chronological order. Wherever possible, avoid cumulated references in order to acknowledge the contribution of each reference individually.

L. 144: Question: Have the retaining (or ring opening) products been identified and can you estimate their yields from IR spectra?

L. 28: Are there appropriate original papers or reviews available for the topics of wet and dry deposition? The monograph by Peter Warneck: *Chemistry of the natural atmosphere* might be an additional source of detailed information.

L. 122: Question: Can the values, observed for k_4 for the compounds of this study, be listed somewhere, say table 2? Are the wall-loss constants in the corresponding photolysis experiments similar?

L. 144: Question: Have the retaining (or ring opening) products been identified and can you estimate their yields from IR spectra?

Suggestion: The extremely valuable discussion on the potential impact of hydrogen bonds could be extended to other nitro-compounds observed as atmospheric reaction products in polluted and even more so remote regions and to pesticides and herbicides such as pendimethalin, DNOC and metabolites. L. 309: The authors should contact the US EPA or the authors of AOPWIN (Philip Howard, Syracuse, NY) about a possible serious error of the AOPWIN software package.

L. 274-278: (suggestion) => …OH radicals, the Hammett constants for electrophilic addition, σ^+, given by Brown and Okamoto (1958) have been proposed by Zetzsch (1982) and updated by Kwok and Atkinson (1995) to fit to the equation

$\log (k_{add} /cm^3 s^{-1}) = -11.71 – 1.34\ \Sigma\sigma^+$,

where the most negative value of the sum $\Sigma\sigma^+$ has to be considered alone and any interaction among the substituents is neglected.

L. 587: One might draw the attention to the weak, broadened band at 3100 wavenumbers (CAT and MCAT) from the H bond between the OH groups that increases with the influence of the nitro group and improve the figure by separating it into the two components for 4NCAT and 4M5CAT. This is required for a precise determination of the band positions. It would be convenient to repeat the rate constants (or the ratios) of Table 3 in the spectra and beneath the structure in Figure 7 B.

L. 12: …technique => techniques

L. 13: …followed => follows

L. 14: results the => results, the

L. 15-16: => …scaled to atmospheric relevant conditions by NO2 photolysis, were evaluated for 3-nitrocatechol and 5-methyl-3-nitrocatechol:

L. 17: results our => results, our

L. 21: aromatic hydrocarbons. Additional… => aromatic hydrocarbons and discussed with gas-phase IR spectra of the nitrocatechols. Additional…

L. 26: car engines emissions => car-engine emissions

L. 34: => methoxy-phenols, and

L. 34-35, 54-55, 56-57, 132, 205, 219-220, 254-255, 283-284: I feel that an alphabetical order of the references in the text is more justified than a chronological order. Wherever possible, avoid cumulated references in order to acknowledge the contribution of each reference individually.

L. 36 (instead of L. 40): 3.3.1 (Bloss et al., 2005)

L. 40, 41: move “in the case of benzene and toluene” to the end of the sentence

L. 43: => mixture, and

L. 55: => aerosol

L. 60: => concentration can be as high as 820…

L. 64: => by OH radicals..

L. 65: => products, occurrence

L. 76: => made of Quartz…at the

L. 90: => their

L. 91: => and well-known rate coefficients for the reaction with OH radicals..

L. 96: => nm, as shown in….., where..

L. 99: Question: => $H_2C=O$ (formaldehyde), or do you want to indicate the isomerization of CH3O to CH2OH as an intermediate?

L. 115: => *t,*

L. 121: => …has been…..OH-radical scavenger …(a series of three nouns with hyphen)

L. 129-130: => NO: > 99.5%....CO (99.997%

L. 142: => was evaluated to range from about..

L. 143: => Up to 30% of the decays of the….and the…

L. 145: => Table 1 presents the…

L. 156: => nitrocatechols by

L. 158: cut off => override

L. 161-163: => was observed, while…….frequencies…, have been measured.

L. 170: has => have

L. 178: The number of 0.1 requires information about the aerosol density obtained in your experiments?

L. 182: => , this

L. 184: => coefficient

L. 186: You mention nitronaphthalene, so naphthalene and nitronaphthalene might be added to table 3

L. 187: => nitroaromatic

L. 188: Please specify. What do you mean with "same order of magnitude", a similar deactivating effect of the nitro group?

L. 190: => results, we

L. 196 => and the O atom

L. 203: => …by the electron withdrawing effect of NO_2, and in consequence, the weakened O-H bond results in an H atom that is more…

L. 206: => Figure 5, the structures of CAT and 4MCAT..

L. 210: => For the 3NCAT structure, one…

L. 212: => , photolysis..

L 217-218: => ring, as the reactivity…is approximately 5-20 times lower than that of their parent compounds.

L. 219 => their

L. 225-227: => Gas-phase reactions….lead to…. In the gas-phase oxidation of..

L. 234: => its

L. 237: => from the..   According to Figure A, the …

L. 250: cancel “compound”

L. 252-253:   groups and considering….., the rate coefficient

L. 256: => , the difference

L. 262: => , we

L 264: => nitrocatechols, the

L. 281: …substituents, another..

L. 285: => , a rate coefficient that is..

L. 289: AOPEWIN => AOPWIN

L. 291: => nitrobenzenes

L. 294: fits => fit

L. 299: = considered

L. 300: => σ^+ for the OH oriented in…..molecules,

L. 305: => , this

L. 306: => , no

L. 309, 311: => $\Sigma\sigma^+$

L. 316: => groups

L. 317: => , the SAR estimations assign the NO2 group substituent factors of Brown and Okamoto (1958) of ….

L. 321: differences => different ratios of ….. 5M3NCAT, the

L. 322: => consistent

L. 323: => SAR models

L. 326: => substituent

L. 330: => proposed

L. 334: => based on the study by Jenkin et al. …..to use a value of 0.5 as new parameter…for the deactivated

L. 336: => In this case, the

L. 337: => ..importance and will

L. 339=> ..nitroaromatic……in order to evaluate all…

L. 344: => sink, being

L. 347: undertake => undergo

L. 350: initiated by OH radicals.

L. 354: of intramolecular

L. 355: E-effect of the NO2 group.

L. 559, 568, 573, 589: => reference (figs. 1 -4

L. 563: => radical

L. 607: hour => h

L. 614: => and SAR-estimated cate coefficients….with OH radicals.

References:

Add subscripts where required (L. 397, 404, 405, 475, 516, 538), add missing DOIs

Complete the references Bejan, I.G. (2006/7) (PhD thesis?) and Prinn et al.

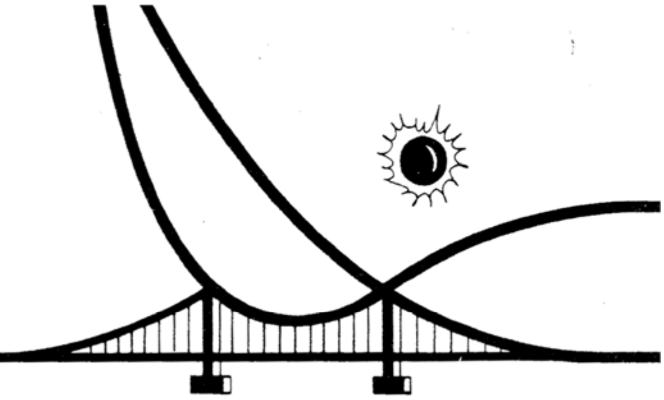
Remove capitals in the title of Finewax et al. (journal name ?), same in L. 487, 488, 493, 494,

Finlayson-Pitts and Pitts: remove abbreviated title of monograph

Harrison et al.: correct initials of Olariu

Typos in names: Henry’s, Simoneit, Dibb

XV
INFORMAL CONFERENCE ON PHOTOCHEMISTRY



ABSTRACTS

STANFORD, CALIFORNIA
JUNE 27 - JULY 1, 1982

CO-CHAIRMEN: D. M. GOLDEN & T. G. SLANGER

XV th Informal Conference on Photochemistry, 27.6.-1.7.82, Stanford,USA

PREDICTING THE RATE OF OH-ADDITION TO AROMATICS USING σ^+-ELECTROPHILIC SUBSTITUENT CONSTANTS FOR MONO- AND POLYSUBSTITUTED BENZENE

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Rate constants were determined for the reactions of OH with aromatics at room temperature in the gas phase: biphenyl, chlorobenzene, benzonitrile, and nitrobenzene. The reactions were studied using the pulsed flash photolysis-resonance fluorescence technique.

Reactants were dosed under slow flow conditions by means of a gas saturation system. Concentrations of reactants and water vapor were calculated from known vapor pressure equations. Verification by freezing the vapors in cold traps always yielded agreement within better than 5%. This technique enables us to dose very low-volatile substances; substances with vapor pressures down to 10^{-2} torr (at room temperature) have been dosed successfully.

Rate constants were determined under pseudo first order conditions. Flash energies ranging from 3-25 J were applied, the former corresponding to initial concentrations of OH $\sim 5 \times 10^{10}$ cm^{-3}. The rate constants obtained were independent of flash energy, water concentration , or inert gas pressure (above 100 torr Ar or He). Rate constants, k , are obtained from linear regressions of the decay rate, τ^{-1}, vs the reactant concentrations; three standard deviations, 3σ, are given in the following Table I to indicate the reproducibility of the measurements:

Tab. I : Rate constants determined in the present study

Aromatic	$(k \pm 3\sigma) / 10^{-12}\ cm^3 s^{-1}$
Biphenyl	5.8 ± 0.8
Chlorobenzene	0.67 ± 0.05
Benzonitrile	0.33 ± 0.03
Nitrobenzene	0.21 ± 0.05

The reactivities of various substituted aromatics increase rapidly with decreasing ionization potential of the reactant molecules.
Table II contains a summary of the data[1-5], in the case of differing values an average value was chosen. The rate constants from Table II can be correlated to the ionization potential[6], yielding the equation

$\log(k/cm^3 s^{-1}) = 0.74 - 1.36\ (IP/eV)$ with a correlation coefficient of $r = 0.95$, if the data points for benzaldehyde, the cresols and chlorinated aromatics are omitted[7).

A somewhat more general correlation is obtained in the present work when using the electrophilic substituent constants, σ^+, after Brown and Okamoto[8) with the following additional rules:

1. Steric hindrance is neglected, the electrophilic substituent constant of the ortho-position is set equal to the constant for the para-position.
2. The total substituent constant, $\Sigma\sigma_i^+$, is the sum of all substituent constants, σ_i, of the substituents, i, connected to the aromatic ring.
3. The OH radical adds to the position with the most negative value for $\Sigma\sigma_i^+$, preferably a free position.
4. If all positions are occupied, the ipso-position is treated like a meta-position.

The result of this treatment of the data in Table II is shown in Figure 1. Using rule 1 the equation

$$\log\ (k/cm^3 s^{-1}) = -11.7 - 1.41\ \sigma^+ \qquad (I)$$

is obtained for the monosubstituted aromatics (dashed line in Figure 1), using rules 1-4 the equation

$$\log\ (k/cm^3 s^{-1}) = -11.6 - 1.39\ \Sigma\sigma_i^+ \qquad (II)$$

is obtained for all aromatics contained in Table II (solid line in Figure 2), the only omitted data set being benzaldehyde, where the main reaction step might be abstraction of the aldehydic H.

Equation II is found to predict aromatic reactivities against OH within a factor of 2, as shown in the diagram, Figure I.

Acknowledgement

This work was supported by the Bundesminister für Forschung und Technologie and by the Fonds der Chemischen Industrie. The author wishes to thank the students M. Ramdohr †, U. Meier, R. Vogelsang, and J. Hurley for performing the measurements.

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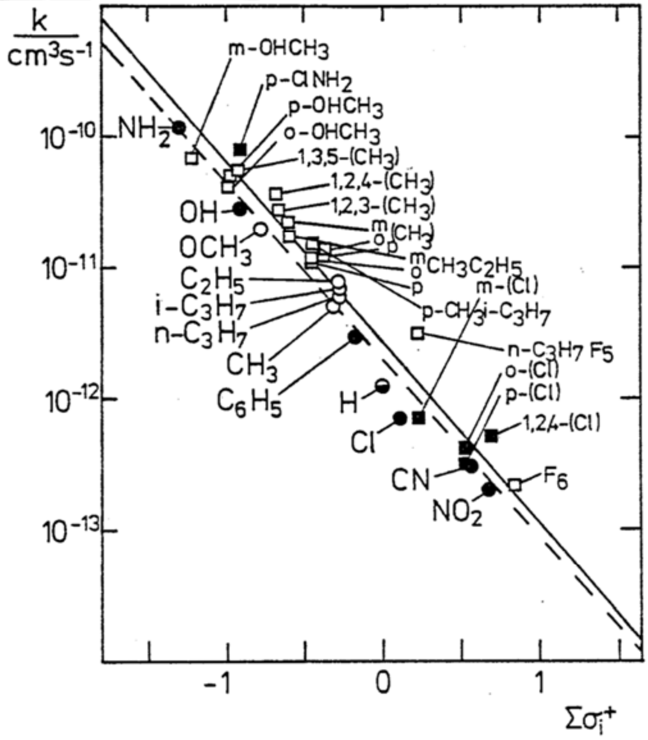

Fig. 1:

Hammett equation correlation for rate constants of OH in the gas phase using σ^+-constants after Brown and Okamoto. Circles, monosubstituted (dashed line), squares, polysubstituted benzene. Filled symbols are work from our laboratory, the solid line includes all data points shown in the figure

Tab. II: Rate constants, k, for the reactions of OH with aromatics at room temperature, electrophilic substituent constants, σ_i^+, and ionization potentials, IP

Aromatic	σ_i^+		σ_i^+		$\Sigma\sigma_i^+$	IP/eV	$k/10^{-12}cm^3s^{-1}$	Ref.
1 Aniline	-1.3	(pNH$_2$)			-1.3	7.69	120	4
2 p-Chloroaniline	-1.3	(pNH$_2$)	+0.399	(mCl)	-0.901	7.77	81	5
3 Anisol	-0.778	(pOCH$_3$)			-0.778	8.21	20	1
4 Biphenyl	-0.179	(pC$_6$N$_5$)			-0.179	8.23	5.8	this work
5 1,2,4-Trimethylbenzene	-2x0.311	(pCH$_3$)	-0.066	(mCH$_3$)	-0.688	8.27	35	1
6 1,3,5-Trimethylbenzene	-3x0.311	(pCH$_3$)			-0.933	8.40	52	1
7 p-Xylene	-0.311	(pCH$_3$)	-0.066	(mCH$_3$)	-0.377	8.45	12	1
8 1,2,3-Trimethylbenzene	-2x0.311	(pCH$_3$)	-0.066	(mCH$_3$)	-0.688	8.48	27	1
9 Phenol	-0.92	(pOH)			-0.92	8.50	28	4
10 m-Xylene	-2x0.311	(pCH$_3$)			-0.622	8.56	22	1
11 o-Xylene	-0.311	(pCH$_3$)	-0.066	(mCH$_3$)	-0.377	8.56	12	1
12 n-Propylbenzene	-0.295	(pC$_2$H$_5$)			-0.295	8.72	5.8	1
13 i-Propylbenzene	-0.28	(p iC$_3$H$_7$)			-0.28	8.73	6.7	1
14 m-Ethyltoluene	-0.295	(pC$_2$H$_5$)	-0.311	(pCH$_3$)	-0.606	-	18	1
15 o-Ethyltoluene	-0.064	(mC$_2$H$_5$)	-0.311	(pCH$_3$)	-0.375	-	13	1
16 p-Ethyltoluene	-0.064	(mC$_2$H$_5$)	-0.311	(pCH$_3$)	-0.375	-	12	1
17 p-Cymene	-0.151	(p iC$_3$H$_7$)	-0.311	(pCH$_3$)	-0.462	-	15	2
18 m-Cresol	-0.92	(pOH)	-0.311	(pCH$_3$)	-1.231	8.75	67	1
19 Ethylbenzene	-0.295	(pC$_2$H$_5$)			-0.295	8.76	7.8	1
20 Toluene	-0.311	(pCH$_3$)			-0.311	8.82	5.5	1
21 o-Cresol	-0.92	(pOH)	-0.066	(mCH$_3$)	-0.986	8.93	47	1
22 p-Dichlorobenzene	+0.114	(pCl)	+0.399	(mCl)	+0.513	8.94	0.33	5
23 p-Cresol	-0.92	(pOH)	-0.069	(mCH$_3$)	-0.986	8.97	52	1
24 Chlorobenzene	+0.114	(pCl)			+0.114	9.06	0.67	this work
25 o-Dichlorobenzene	+0.114	(pCl)	+0.399	(mCl)	+0.513	9.07	0.42	5
26 1,2,4-Trichlorobenzene	+2x0.114	(pCl)	+0.399	(mCl)	+0.627	9.10	0.52	4
27 m-Dichlorobenzene	+2x0.114	(pCl)			+0.228	9.12	0.69	5
28 Benzene	0				0	9.24	1.2	1
29 Benzaldehyde	+0.36	(mCHO)			+0.36	9.53	16	3
30 Benzonitrile	+0.562	(mCN)			+0.562	9.71	0.33	this work
31 Hexafluorobenzene	-3x0.073	(pF)	+3x0.352	(mF)	+0.837	9.90	0.22	1
32 Nitrobenzene	+0.674	(mNO$_2$)			+0.674	9.90	0.21	this work
33 n-Propylpentafluorobenzene	-0.064 -3x0.073	(mC$_2$H$_5$) (pF)	+2x0.352	(mF)	+0.421	-	3.1	1