

A Crystallographic Scale of Carbon Acidity

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For several carbon acids C–H, mean C–H...O distances in 551 crystal structures correlate well with conventional $pK_a(\text{Me}_2\text{SO})$ values, thus furnishing a new scale of carbon acidity.

The measurement of carbon acidities is of fundamental importance in physical organic chemistry.^{1–3} In this communication, we describe a scale of acidity which is based on one of the most direct manifestations of this property, namely the distance to which a C–H group is able to attract an O atom.

This scale is calibrated in terms of C–H...O hydrogen bond distances in crystals⁴ and hence we term it a crystallographic scale of carbon acidity.

There is evidence that the lengths of X–H...O (X = C, N, O) hydrogen bonds depend on the acidity of the X–H group

rather than on O atom basicity.⁵ Earlier studies on chloroform derivatives,⁶ alkenes and alkynes⁷ have shown that the more acidic a particular type of C–H group, the shorter, in general, are the C–H···O bonds it forms. However, C–H···O bonds are very weak when compared with O–H···O and N–H···O bonds and there is much scatter in experimental C···O distances. Accordingly, any conclusions based on these distances can be drawn only from large samplings of crystallographic data. The effectiveness of the Cambridge Structural Database (CSD)⁸ in carrying out such exercises becomes immediately obvious. The large number of accurate crystal structures in the CSD means that the distorting effects on the C···O distances caused by different environmental effects in individual crystal structures will tend to cancel out and may be regarded as random errors. O atom basicity for instance, which in any case only changes C···O distances marginally, can be neglected completely.

The 1990 update of the CSD (82 129 entries) was used. Non-metal atom containing crystal structures obtained from diffractometer data with *R*-factors ≤ 0.10 were chosen and duplicate refcodes and structures with errors or disorder were rejected. All the chosen structures contain O and were categorised according to the functional groups shown in Table 1. For non-oxygenated compounds such as CHCl₃, CH₂Cl₂, RRCH(CN) and RCH(CN)₂, the O atom is present in a second molecular residue within the crystal. Each compound was inspected manually (using the graphics feature in version 4 of the CSD) and the detailed break-up into functional groups based on extra electronegative α -substituents, *etc.*, was made on this basis. For example R–(CO)C \equiv C–H, R–C \equiv C–H and RRC(OH)–C \equiv C–H were taken as separate groups. A total of 1314 hits was obtained eventually. Of these, 551 compounds were found to contain 1000 C–H···O bonds according to the following criteria which were evaluated using the program GSTAT90. The positions of the H-atoms were normalised and a C–H···O bond was assumed to exist in those cases where the

C···O distances *D*, the H···O distance *d*, and the C–H···O angle θ are such that $2.8 \leq D \leq 4.0 \text{ \AA}$, $2.0 \leq d \leq 3.0 \text{ \AA}$, and $110 \leq \theta \leq 180^\circ$. These ranges have been discussed and justified previously.⁴ The mean values of *D* and θ for the 1000 C–H···O bonds in the various functional groups are given in Table 1 and serve as the basis for our scale of carbon acidity.

Fig. 1 is a plot of the mean *D* values vs. the mean p*K*_a values in Me₂SO for representative compounds within each of the functional groups considered. As many Me₂SO p*K*_a values for chemically related compounds were chosen as was convenient.^{1,2} For compounds of the type RRCH–NO₂, for example, the average p*K*_a of the two compounds MeNO₂ (17.2) and Me₂CHNO₂ (16.8) was taken. In those cases where Me₂SO p*K*_a values were unavailable, because of anion instability or any other reason, the gas phase values ΔH° were converted into the equivalent Me₂SO values using a calibration curve.^{3,9} Since these two scales are related in a linear fashion,² this procedure is acceptable. Any particular compound almost never figured in the calculation of both the *D* value and the p*K*_a value. This is neither particularly surprising nor is it a problem as far as devising a new acidity scale is concerned. Fig. 1 shows two broad categories of carbon acids. When the C–H groups have single atoms as α -substituents (CHCl₃, CH₂Cl₂), are part of an sp² system (RRC=CH–NO₂, H₂C=CHR) or are otherwise sterically unhindered (RC \equiv C–H, RCHRCN, RCHO; ● in Fig. 1), the C···O distances are well correlated with the p*K*_a values for the respective substituent group (correlation coefficient, *r*, 0.95). This correlation is as good as that between Me₂SO and gas phase acidities (*r*, 0.94). When the C–H moiety is part of a bulkier substituent group, however, the mean C···O distances are restricted to a narrow range between 3.38 and 3.52 Å [(RSO₂)₂CHR, RRCH–NO₂, (RCO)₂CHR; ▲ in Fig. 1]. The entire study was repeated, plotting the Me₂SO p*K*_a values vs. the mean of the lowest quartile of the C···O distances in the range 2.8–4.0 Å, in the expectation that there would be less interference from ‘van der

Table 1 C–H···O bond properties and p*K*_a (Me₂SO) values for some carbon acids

Functional group	No. of compounds ^a		Total no. of C–H···O bonds	Mean ^b		p <i>K</i> _a (Me ₂ SO)
	Retrieved	With C–H···O bonds		C–H···O length/Å	C–H···O angle/°	
CHCl ₃	38	16	19	3.21(3)	147(4)	20.0
CH ₂ Cl ₂	29	15	35	3.39(3)	142(2)	33.8 ^c
RCHO	276	102	165	3.49(1)	139(5)	44.5 ^c
H ₂ C=CH(R)	179	101	238	3.58(1)	143(1)	49.5 ^c
RC \equiv CH	30	14	17	3.39(5)	141(4)	36.3 ^c
R(CO)C \equiv CH	8	7	7	3.26(3)	166(2)	24.9 ^c
RRC(OH)C \equiv CH	58	25	34	3.42(4)	149(3)	28.7
RCH(R)CN	141	63	101	3.43(2)	138(2)	31.3
PhCH(R)CN	12	3	4	3.26(6)	140(4)	21.9
R(CO)CH(R)CN	9	5	16	3.38(3)	129(4)	10.2
RSO ₂ CH(R)CN	4	4	12	3.39(3)	130(3)	12.0
(CN) ₂ CH(R) ^d	1	1	1	3.07	131	11.0
(CN) ₂ CH(R) ^e	4	4	14	3.38(5)	144(5)	11.0
RRC=CHNO ₂	18	10	11	3.46(4)	147(4)	25.5 ^c
RRCH–NO ₂	120	82	159	3.46(1)	142(1)	17.0
Ar ₂ CH(R)	246	31	36	3.68(3)	151(2)	32.2
Ar ₃ CH	13	1	1	3.62	131	30.6
(RSO ₂) ₂ CH(R)	10	7	24	3.40(4)	140(3)	12.5
R(CO)CH ₂ COR	8	6	8	3.52(5)	136(6)	13.3
R(CO)CH(R)COR	25	8	8	3.57(7)	140(5)	15.1
R(CO)CH(R)CO ₂ R	36	19	41	3.50(2)	140(3)	14.0
A ^f	8	3	5	3.25(4)	132(4)	7.4
B ^f	41	24	44	3.49(3)	137(2)	11.2

^a All compounds contain oxygen in one or more molecular residues. ^b E.s.d.s in parentheses. ^c Converted from gas phase value.

^d Unclathrated compound. ^e All compounds. ^f See Fig. 1.

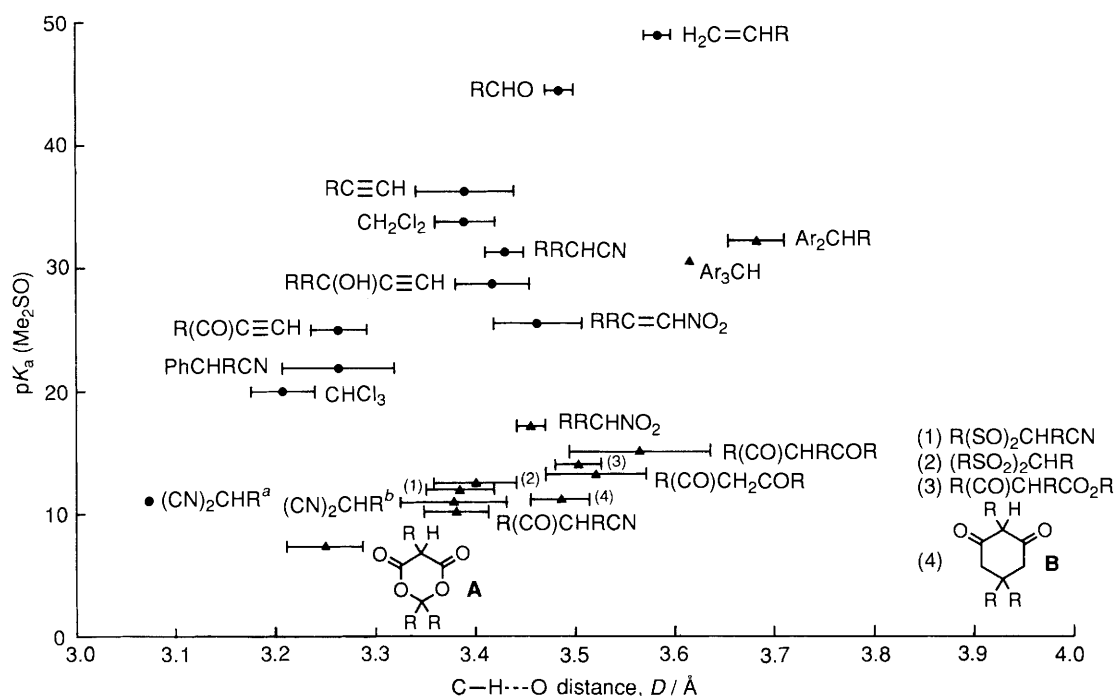
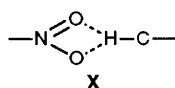


Fig. 1 Plot of C-H...O distances, D , vs. $pK_a(\text{Me}_2\text{SO})$ for the functional groups in this study. Sterically unhindered carbon acids are shown as \bullet while for those marked \blacktriangle , the approach of the C-H and O groups is more difficult. For $(\text{CN})_2\text{CHR}$ compounds, (a) represents a single unclathrated structure while (b) represents the average of all structures.

Waals-like' contacts. Yet, the correlation was no better than when all the C...O distances were used. This is further confirmation of the long-range distance characteristics of the C-H...O hydrogen bond which is an essentially electrostatic interaction.⁴

All these observations suggest that mean C...O distances in the crystal are a good measure of carbon acidity when there is little or no steric hindrance to the approach of an O atom to a C-H group. When such steric hindrance exists, the mean approach of O does not fully reflect the acidity of the group since there seems to be a minimum cut-off distance around 3.4 Å. Even so, there are variations. Contacts to the extremely acidic but also sterically bulky 1,3-dioxane-4,6-dione group are very short (*ca.* 3.25 Å) and electronic factors seem to outweigh steric ones. In contrast, when steric hindrance is excessive, the mean D values are greater than 3.50 Å [(RCO)₂CHR 3.57 Å; Ar₃CH, 3.62 Å]. C...O contacts which involve CH₂(CN)₂ or NO₂ substituents are noteworthy. Of a total of 14 contacts involving CH₂(CN)₂, 13 are found in crown ether clathrates and the C...O distances are unusually long, perhaps because of the rigid dimensions of the host molecule. In one compound, (BOTROR),¹⁰ however, the CH₂(CN)₂ molecule is not clathrated and forms a very short C...O contact of 3.07 Å, fully reflective of its carbon acidity. Again C...O contacts to RRC=CH-NO₂ and RRCH-NO₂ groups are slightly longer than might be expected, partly because of steric factors and partly because many C-H...O bonds are bifurcated, that is they are of the type X, which tends to lengthen the contact distance.



These limitations aside, it seems that this crystallographic scale for carbon acidity is of general applicability. Such a scale, being totally different from existing ones, would be com-

plementary to them and could be used for compounds which are not amenable to the more conventional methods. These include species with unstable anions, reactive substances whose X-ray structures have been determined under special conditions, organometallics and cluster compounds. Since the scale has been obtained from a database of ever-increasing size and accuracy, the numerical values so obtained are also likely to become more reliable in the future.

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