electrons are transferred continuously in the external circuit to the cathode where H^+ is discharged as H_2. The Ti^{3+} ion near the surface may therefore be expected to be largely ionized leaving an active chemical species of the type Ti^{4+}-OH·. The very high turnover number for O_2 evolution suggests that O_2 is not produced directly from the decomposition of these species, because this would require the rehydroxylation of the surface afterward, which, from what is known about the surface chemistry of many oxides, is a slow process even when a large excess of water is present. Possibly, only physisorbed water is decomposed, according for instance to a charge-transfer process of the type

$$Ti^{4+}\text{-}OH\cdot + (HOH)_{ads} \rightarrow Ti^{4+}\text{-}OH^- + OH\cdot + H^+ \quad (4)$$

followed by

$$2OH\cdot \rightarrow H_2O_2 \rightarrow \tfrac{1}{2}O_2 + H_2O \quad (5)$$

Although no direct evidence for this mechanism exists to our knowledge, it is significant that OH radicals[7] and H_2O_2[8] have been detected upon irradiation of TiO_2 in water.

Actually, very little perturbation of the surface structure would be involved with such a model. The surface OH groups of the solid are not decomposed but simply act as intermediates for charge trapping and charge transfer.

On the other hand, at the GS interface, the evidence points to the direct decomposition of the surface OH groups. Boonstra and Mutsaers[5] have shown that the surface OH groups of TiO_2 can, upon illumination, hydrogenate acetylene and ethylene. As pointed out by Schrauzer and Guth themselves, there seems to be no conceptual difference between this process and the reduction of nitrogen or the formation of H_2 when no reducible substrate is available. Moreover, Schrauzer and co-workers have also shown that the decomposition of several hydroxides is photoassisted in the near-UV.[9] H_2 is evolved and reducible substrate such as N_2 are reduced, when present. These reactions, however, are not catalytic with respect to the hydroxide and it seems logical to relate them to the photoassisted decomposition of the hydroxylated surface layer on TiO_2. In addition, the fact that in the GS experiments H_2 is produced on the same surface as O_2 requires that reducing chemical species be generated at some intermediate level near the oxidizing species. Most probably, these reducing species at the surface are derived from the donor centers which, owing to the absence of electron flow in an external circuit, would be much less ionized than in the LS systems. According, to these considerations, O_2 and H_2 could be produced from the following decomposition reactions:

$$2Ti^{3+}\text{-}OH\cdot \rightarrow 2Ti^{3+}\square + H_2O + \tfrac{1}{2}O_2 \quad (6)$$

$$2Ti^{3+}\square + H_2O \rightarrow Ti^{4+}\text{-}O\text{-}Ti^{4+} + H_2 \quad (7)$$

It may be significant that Ti^{3+}-exchanged Zeolite A has recently been shown to yield hydrogen when bathed in water under visible illumination of any wavelength.[10] This suggests that step 7 as well as 3 is also photoassisted.

Compared with the previous model, this reaction scheme requires much more severe surface modifications, particularly for generation (step 6) of the reducing species. $Ti^{3+}\square$.

Moreover, in order to make the process cyclic, hydrolysis of the right-hand member of eq 7 is necessary. As pointed out before, this may be expected to be a slow reaction, and additionally provides a mechanism for irreversible sintering of the oxide.

Some spectroscopic information is available on the nature of the species produced by light on the surface of TiO_2 in GS system. Gravelle et al.[11] have shown by ESR spectroscopy that surface Ti^{3+} ions are produced upon evacuation in the dark at moderately high temperature of an hydroxylated surface and that the same species can also be formed by UV irradiation at room temperature. Later, Lo et al.[12] confirmed by various electron spectroscopic techniques that a Ti^{3+}-rich monolayer is formed under illumination. Furthermore their data suggested that the presence of Ti^{3+} ions on the surface is necessary for the chemisorption of H_2O. Lo et al. did not study the efficiency of the rehydroxylation process in successive rehydration treatments under illumination, but Primet et al.[13] have shown that the rehydroxylation of a thermally dehydroxylated TiO_2 surface with H_2O vapor was not a truly reproducible process; it was, however, more reproducible for crystalline material than for high surface area amorphous material; the data were taken as evidence of surface reconstruction. We note here that the system should be more stable when TiO_2 is immersed in liquid H_2O than when subjected to alternative dehydroxylation-rehydroxylation cycles, a process known to favor sintering. Although the thermal dehydroxylation of the TiO_2 surface is certainly not identical with its photodecomposition, it seems reasonable to assume that surface reconstruction also occurs in the latter case and that it may be responsible for the loss of activity. Interestingly, it may be this surface chemistry which limits the catalytic efficiency of the gas-solid reactions, rather than electronic considerations.

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Computer Retrieval and Analysis of Molecular Geometry.[1] 4. Intermolecular Interactions

Sir:

Intermolecular forces are often described by the sum of isotropic atom-atom potentials[2] and this approach has been widely used in predicting the packing in molecular crystals.[3] However, it has been suggested by several authors[4] that the heavier p-block elements can form relatively strong directional interactions with nucleophiles for which several terms have been used such as "donor-acceptor interactions",[4a] "secondary bonding",[4b] and "incipient nucleophilic attack".[5] A convincing demonstration of the directional nature was given by Rosenfield, Parthasarathy, and Dunitz[5] for the system X—S(Y)···N

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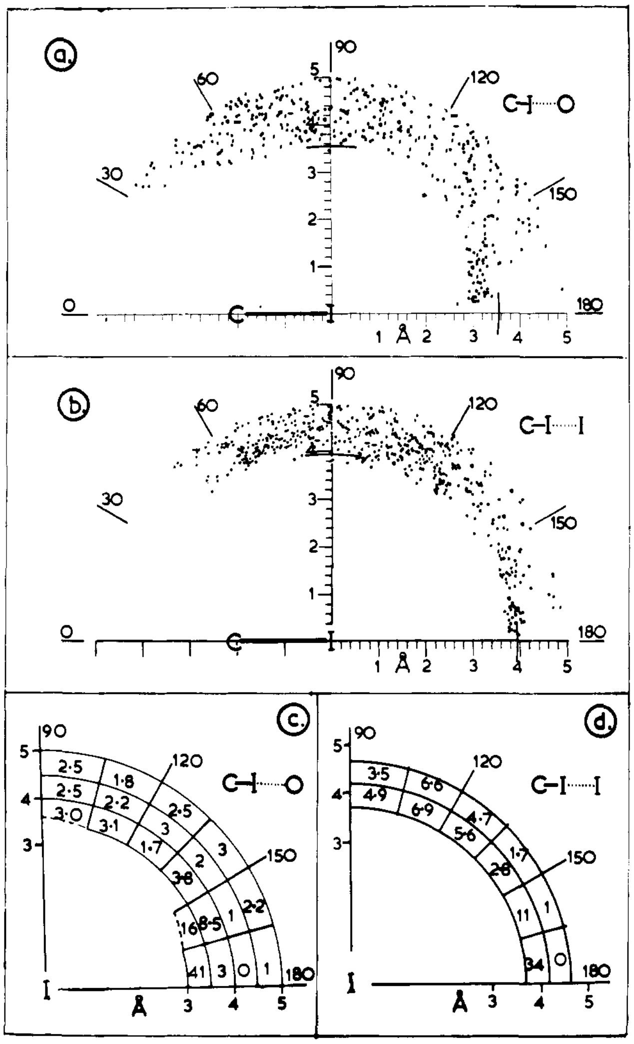

Figure 1. (a) A polar scatterplot of C—I···O contacts (r) <5 Å against the C—I···O angle (θ). An average C—I bond is superimposed with I at the origin, and the small arcs at $\theta = 90$ and 180° represent the conventional sum of the van der Waals radii (3.55 Å[4a]). (b) Polar scatterplot of C—I···I contacts (r) (excluding I^-) <5 Å against the C—I···I angle (θ). The sum of the van der Waals radii is 3.95 Å.[4a] (c) Density (per unit volume) of oxygen atoms near a C—I bond derived from (a). The compartments represent annuli around the C—I axis at intervals of 15 and 0.5 Å in the region $\theta = 90$-180° and $r = 3.5$-5.0 Å. (d) Density of iodine atoms near a C—I bond derived from (b). The ranges are $\theta = 90$-180°, $r = 3.4$-4.7 Å.

where the nucleophile N almost always formed a nearly linear X—S···N arrangement, even up to an S···N distance of 4 Å.

Here we report a technique for the automatic retrieval and analysis of intermolecular contacts for organic molecules. The Cambridge Crystallographic Data Centre[6] has produced a machine-readable file containing all published atomic coordinates for crystal structures of organic molecules. Using their programs[7] it is possible to retrieve structures containing any intra- or intermolecular bonding (defined by distance ranges) and to tabulate the geometrical data[1] automatically. Here we present the application of these computer techniques to intermolecular interactions involving C—X bonds (X = Cl, Br, I) and produce a quantitative picture of many of the ideas of Bent[4a] and others.

Since many molecular crystals (especially of steroids[8]) have been shown to have short C—Br···O and C—I···O interactions we have concentrated on the geometrical arrangement of O atoms around C—X bonds. We found 219 crystal structures[9] of molecules containing oxygen and with a C—I bond. For those with published coordinates all intermolecular I···O contacts <5 Å were calculated along with the C—I···O angle. Although some compounds had no I···O distances in this range, many had several, and over 500 contacts were found, as shown in the scatterplot (Figure 1a). Several features are immediately apparent. There is a relatively sharp boundary (±0.1 Å) for nonbonded contacts which, although varying smoothly with the C—I···O angle, is far from isotropic. At 90° the minimum I···O distance is 3.6-3.7 Å, whereas at 180° it is as low as 2.8 Å. After a geometrical correction[10] has been applied to correct for the different annular volumes, the density of points is strikingly nonuniform (Figure 1c). At $\theta = 90°$ the radial distribution density is essentially uniform, whereas at $\theta = 180°$ it varies by about two orders of magnitude from $r = 3.2$ to 4.2 Å. The angular distribution changes equally dramatically from $\theta = 135$ to 180°.

Similar, but not so pronounced, results were found for C—Br···O contacts and C—Cl···O contacts, with over 3000 examples for each.[11] For Br $r_{\min}$ ($\theta = 90°$) was ~3.4 Å, while $r_{\min}$ ($\theta = 180°$) was ~2.9 Å. The increase in density of points at 3.0 Å and 180°) over that at 3.5 Å and 90° was about seven times, but the "void" at 4.2 Å and 180° was much less pronounced. For Cl the effects were smaller but still observable. To find out whether the distribution was independent of the chemical nature of the oxygen group the C—I···O examples were subdivided into C—I···O (ketone), C—I···O (ether), C—I···O (ester carbonyl), and C—I···O (ester C—O—C). There were no striking differences between the plots, suggesting that Figure 1a is representative of a wide range of different chemical types.

Figure 1b shows an analogous plot for the C—I···I system where over 400 examples were found. As might be expected the minimum contact distance (3.7-3.8 Å) is now essentially independent of angle. However, the density of points is still markedly anisotropic with a factor of about seven between (3.7 Å and 90°) and (3.7 Å and 180°) and a well-defined "void" at 4.4 Å and 180°.

Although for each individual structure the intermolecular contacts will be determined by a complex mixture of attractive and repulsive forces, we feel that, because of the large number and varied chemical type of compounds, Figures 1a and 1b reflect features of the C—I···O and C—I···I potential energy surfaces.[12]

We can suggest qualitative differences between the C—I···O potential surface at $\theta = 90$ and 180°. The former is relatively shallow and broad, whereas the latter has a sharper, deeper minimum at a shorter I···O distance. A configuration at the "void" (4.2 Å and 180°) is presumably relatively less stable than most others in the range 3.5-5 Å.[15] Beyond 5 Å the distribution of points will be affected by other atoms making closer contacts to iodine.[16] These features of the energy surface are qualitatively valid also for C—Br···O and C—Cl···O, although the minimum at $\theta = 180°$ becomes progressively shallower and broader. Even for C—I···I, which shows an isotropic repulsive potential, there is a global minimum at (3.9 Å and 180°) which rises sharply on both sides.

Because so many crystal structures (over 20 000) are now in computer-readable form, the study of the variability of intermolecular geometry becomes possible. Some configurations may represent incipient chemical reaction[13] (e.g., two points at 3.1 Å and 0° for the C—Br···O system (not shown) correspond to nucleophilic attack of oxygen at the carbon of CBr). The study of the environment of groups should lead to better intermolecular potentials.

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(11) These studies would have taken several man-years by manual methods (literature searching, punching coordinates, and checking errors) but required only ~10 min computer time altogether on an IBM 370/165.

(12) Geometrical correlations have been linked to the potential energy surface of molecules (ref 13). A similar argument has been used by Brown[14] who plotted O—H---O interactions and suggested that the high frequency of occurence of linear arrangements corresponds to a potential minimum.

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(16) In several cases in Figure 1a the iodine makes contact with two oxygen atoms of a neighboring molecule (e.g., an ester).

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Small Errors in C-H Bond Lengths May Cause Large Errors in Rotational Correlation Times Determined from Carbon-13 Spin-Lattice Relaxation Measurements

Sir:

Measurements of spin-lattice relaxation times (T_1) of resonances of proton-bearing carbons in proton-decoupled ^{13}C NMR spectra have been used extensively to study rotational motions of large molecules in solution.[1,2] Because ^{13}C-^{1}H dipole-dipole interactions with directly bonded hydrogens provide an overwhelmingly dominant relaxation mechanism[2] (even at high magnetic field strengths[3]), it is necessary to know the values of the pertinent carbon-hydrogen bond lengths (r_{CH}) in order to extract values of rotational correlation times (τ_R) from the measured T_1 values.[1,2] In this report we show that the widespread practice of setting r_{CH} = 1.09 Å (a typical value obtained from rotational spectroscopy) can cause very large errors in the value of τ_R. We show that small errors (2-3%) in the assumed value of r_{CH} can result in values of τ_R in error by as much as a factor of 2. This sensitivity of τ_R to the choice of r_{CH} is caused by the *combined* effects of the dependence of $1/T_1$ on $r_{CH}{}^6$ and the nonlinear relationship between $1/T_1$ and τ_R (when dealing with large molecules at typical magnetic field strengths; see Figure 1).[4] We show that the temperature dependence (at 14.2 kG) of the T_1 values and nuclear Overhauser enhancements (NOE) of the α-carbon resonances of aqueous hen egg-white lysozyme can be used to determine τ_R *and* r_{CH}. We discuss the choice of magnetic field strength for maximizing the accuracy of τ_R when r_{CH} is not known accurately. We show that the reported discrepancies between τ_R values measured at 14.2 and 63.4 kG[5] are eliminated (without invoking anisotropic rotations[5] or internal librational motions[6]) when the corrected value of r_{CH} is used.

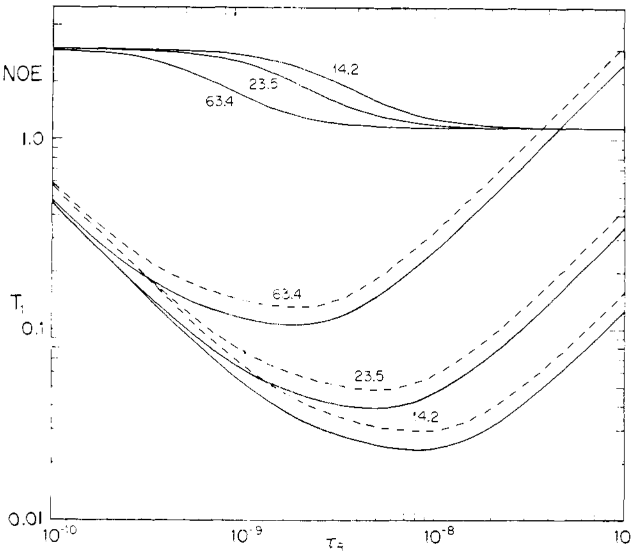

Figure 1. Semilog plots of theoretical T_1 (in seconds) and NOE (ratio of intensities with and without proton decoupling) vs. τ_R (in seconds) for a ^{13}C spin undergoing ^{13}C-^{1}H dipole-dipole relaxation, in the case of isotropic rotational reorientation and under conditions of proton decoupling.[4] Plots are given for various magnetic field strengths, indicated in kilogauss. The NOE values are independent of the choice of the carbon-hydrogen distance.[4] The T_1 plots were computed for a C-H group with r_{CH} = 1.09 (solid curves) or 1.13 Å (dashed curves).

The appropriate choice of r_{CH} for the interpretation of ^{13}C relaxation data is the average $\langle r^{-3}\rangle^{-1/3}$ for the vibrational ground state.[7] Only a few determinations of rotational motions from ^{13}C T_1 measurements have incorporated vibrational corrections for r_{CH}.[7,8] These estimates indicate that $\langle r^{-3}\rangle^{-1/3}$ may be 1-2% greater than r_{CH} values based on rotational spectra or electron diffraction data.[7,8] In addition, results from NMR spectroscopy in liquid crystal solvents (which yields distance parameters related to $\langle r^{-3}\rangle^{-1/3}$) suggest that, at least in some cases, the vibrational correction may be >2%.[9] Furthermore, the reported frequency dependence of some ^{13}C T_1 values has been used to suggest a value as large as 1.15 Å for the C^{α}-H bond length in some peptides.[10]

Consider a carbon (with a single directly bonded hydrogen) which is part of a molecule undergoing isotropic rotational reorientation with a correlation time τ_R. Figure 1 shows theoretical plots of T_1 and NOE vs. τ_R (in a range of τ_R values expected for molecular weights between 10^3 and 10^6), at 14.2, 23.5, and 63.4 kG.[4] The NOE values are independent of the choice of r_{CH}. For the T_1 computations, r_{CH} values of 1.09 (solid lines) and 1.13 Å (dashed lines) were used. Let us assume that the true values of r_{CH} and τ_R are 1.13 Å and 8 ns, respectively. Then the measured T_1 at 14.2 and 63.4 kG will be 29.6 and 270 ms, respectively. If we use r_{CH} = 1.09 Å in the interpretation of the data, Figure 1 will yield τ_R values of 18 ns (14.2 kG) and 10 ns (63.4 kG).[11] Clearly, if the true $\tau_R \approx$ 8 ns, an erroneous choice of r_{CH} is much more serious for T_1 data at 14.2 kG than for data at 63.4 kG. In general, measured T_1 values which are near the minimum of the T_1 vs. τ_R curve may yield very erroneous values of τ_R, unless r_{CH} is known with great accuracy. The minimum in the T_1 curves occurs at τ_R values of ~2, 5, and 8 ns at 63.4, 23.5, and 14.2 kG, respectively. Values of τ_R in the range 1-10 ns are expected for many substances (in "nonviscious" solvents at room temperature) which have molecular weights in the range 2000 to 20 000.[4,10,12] Clearly, when ^{13}C spin-lattice relaxation times are used for determining the τ_R values of such molecules, it is desirable to choose a magnetic field strength which does not place T_1 near the minimum in the T_1 vs. τ_R plot.

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