PAIR OF PENETRATING PARTICLES OF ENERGY E GREATER THAN 5×10^8 e.V. TRAVERSING LEAD ABSORBER

increases rapidly with decreasing energy. According to Hamilton, Heitler and Peng[6], a proton of this energy can still produce a meson.

I wish to thank Dr. R. L. Sen Gupta for lending the apparatus for the investigation and for his help in the interpretation of the photographs.

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Phase Angle Determination in X-Ray Crystallography

THE extensive programme of work on the extra reflexions caused by thermal motion of the crystal lattice, which has been carried out by Lonsdale and her colleagues at the Davy Faraday Laboratory, has shown that these occur, not rarely as was at first thought, but in all crystalline substances. The technique of experimental observation of these reflexions has been so developed that at the present time an adequate survey of any particular crystal can be made in a reasonable time, using standard laboratory equipment.

The observation has already been made[1] that the shape of the diffuse reflexions gives valuable information regarding the orientation of chain molecules in the unit cell, and this rapidly applicable technique is likely to find increasing use in future analyses. The question naturally arises whether a more detailed study of the diffuse reflexions would give information regarding the phase angles of the parent Bragg reflexions.

In the case of non-centro-symmetric reflexions, no obvious relationship is forthcoming. When the reflexion forms one of a centro-symmetric group, however, its structure factor can be written in the form :

$$F(h,k,l) = \sum_r f_r \cos 2\pi \left(h.\frac{x_r}{a} + k.\frac{y_r}{b} + l.\frac{z_r}{c} \right),$$

and the determination of the phase angle degenerates into the determination of the sign of $F(h,k,l)$. Now using only Bragg reflexions, the only points at which $F(h,k,l)$ is observable are those for which (h,k,l) are integers. If some method of observing the function at intermediate values were available, the changes in sign would be indicated by the vanishing of the function.

The observation of regions of diffuse reflexion provides precisely this information, and, by a careful analysis, the approximate value of $F(h,k,l)$, over large regions of reciprocal space, can be found. Unfortunately, the existence of a point of zero intensity is seldom unequivocal, owing to the presence of other background radiation and only approximate identity of $F(h,k,l)$ and the dynamical structure factor, so that *changes* in sign derived from this technique may be doubtful. In a large number of cases, however, the diffuse connexion is strong enough to make it certain that there is *no* zero of $F(h,k,l)$ in the region of reciprocal space between adjacent Bragg reflexions, and in this case it can be stated that the values of $F(h,k,l)$ have the *same* sign.

It is not suggested that a great number of reflexions can have their phase angles determined by this method, but that a sufficient number may be determinable to make the preliminary stages of a structure analysis a less hazardous operation than is now the case. The usefulness of small numbers of planes with associated phase angles has been demonstrated in the recent work of Boyes-Watson and Perutz on horse hæmoglobin[2]. Although the phase angles determined by the above procedure are only relative (that is, their relation

to the positive term $F(0,0,0)$ is still unknown), this should not lead to difficulty, since a Fourier synthesis, taken in conjunction with known stereo-chemical data, will usually clear up this point.

Through the courtesy of Dr. K. Lonsdale and Mr. P. G. Owston, the method has been applied to hitherto unpublished photographs of oxalic acid-dihydrate. The pairs of planes : $(0,1,11)$, $(\bar{1},0,11)$; $(\bar{4},1,7)$, $(\bar{5},0,7)$: $(5,1,4)$, $(5,0,5)$; $(3,1,0)$, $(4,0,0)$; $(\bar{4},1,9)$, $(\bar{4},0,8)$ and $(1,1,\overline{10})$, $(1,0,\overline{11})$, were found to have definite diffuse connexion, and an examination, using the known atomic co-ordinates, shows that their structure factors have, in each case, the same sign. The author wishes to express his sincere thanks for permission to use these data.
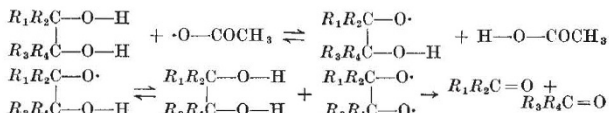
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Glycol Splitting by Hydroxyl Radicals

RECENTLY[1] I suggested, on theoretical grounds, that the splitting of α-glycols to aldehydes or ketones by means of lead tetra-acetate was due to dehydrogenation by free acetate radicals.

$$\begin{array}{l} R_1R_2C{-}O{-}H \\ R_3R_4C{-}O{-}H \end{array} + \cdot O{-}COCH_3 \rightleftharpoons \begin{array}{l} R_1R_2C{-}O\cdot \\ R_3R_4C{-}O{-}H \end{array} + H{-}O{-}COCH_3$$

$$\begin{array}{l} R_1R_2C{-}O\cdot \\ R_3R_4C{-}O{-}H \end{array} \rightleftharpoons \begin{array}{l} R_1R_2C{-}O{-}H \\ R_3R_4C{-}O{-}H \end{array} + \begin{array}{l} R_1R_2C{-}O\cdot \\ R_3R_4C{-}O\cdot \end{array} \rightarrow \begin{array}{l} R_1R_2C{=}O \ + \\ R_3R_4C{=}O \end{array}$$

If this hypothesis is correct, it follows that the free hydroxyl radical, $\cdot$OH, which Haber and Weiss[2], and more recently Baxendale, Evans and Park[3] have shown to be present in Fenton's reagent (hydrogen peroxide plus a ferrous salt), should be capable of acting in a similar way. Fenton[4], however, had shown that his reagent oxidized ethylene glycol to glyoxal and glycerol to either glyceraldehyde or dihydroxyacetone. I have therefore re-examined these reactions, and by using dimedone as a diagnostic reagent, have shown that whereas the main oxidation proceeds :

$$CH_2OH{-}CH_2OH \rightarrow CHO{-}CHO,$$

some formaldehyde is liberated both from ethylene glycol and from glycerol. 2 : 3-Butylene glycol similarly gives acetaldehyde as well as diacetyl, whilst pinacol yields acetone.

In all these cases the extent of glycol fission is enhanced by working in solutions strongly buffered with sodium acetate and acetic acid.

Under Fenton's reaction conditions, which employ reagents in concentrated solution with molecular hydrogen peroxide in large excess, the free hydroxyl radical would have a very short life. Theory indicates that this would be most unfavourable for glycol fission, which requires rather the slow production of free radicals in very low concentration. These positive preliminary results indicate, however, that glycol splitting may be quite a normal reaction of free neutral radicals in solution, and not specifically a reaction of lead tetra-acetate, or of periodic acid ; and further experiments are being conducted to explore the range of reagents which may be used, and the reaction conditions which will favour high reaction yields.

The concurrent formation of both acetaldehyde and diacetyl from 2 : 3-butylene glycol by the action of Fenton's reagent may indicate that both the C—H and the C—O—H groups of alcohols can be dehydrogenated directly by neutral hydroxyl. One of these reactions, however, may be a second-stage process involving molecular hydrogen peroxide ; for example :

$$R_1R_2CH{-}O\cdot + HO{-}OH \rightarrow R_1R_2C{=}O + H_2O + \cdot OH.$$

The formation of acetone from pinacol shows, however, that the primary attack on the C—O—H group of alcohols does occur, and is diagnostic therefore in answering the vexed question[5] of the mode of oxidation of alcohols.

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Polymerization of Methyl Methacrylate

IN a general survey of the polymerization of vinyl compounds using the method previously described[1], we have studied methyl methacrylate, and have found that it presents features of some interest.

Determination of the spontaneous rate of polymerization is difficult since traces of catalyst and inhibitor are formed with great ease either from the monomer or from inseparable impurities. However, the rates of change of viscosity during irradiation (λ 3000–4000 A.) are reproducible, and conform to the kinetic equations given previously, being proportional to $I^{1/2}$ at low intensities, and independent of I at high intensities. Thus we have been able to estimate the velocity constants of chain propagation, transfer and termination with reasonable accuracy. They have the values 150, 0·03 and $1·3 \times 10^7$ moles litre^{-1} sec.$^{-1}$ respectively at 25°. The life-time of a growing polymer chain is about 3 sec.

It will be seen that the values for propagation and transfer are about forty times those of styrene, while termination occurs only