Heat of Sublimation of Carbon

Long and Norrish emphasize in a recent communication¹ the importance of the tetravalent 4S state of the carbon atom from the point of view of organic chemistry, stating that neglect to distinguish between divalent and tetravalent atomic states of carbon is mainly responsible for the apparent state of confusion characterizing at present the thermochemistry of carbon. It may be mentioned that Schmid and Gerö take a similar view in the thermochemical interpretation of their results concerning the spectrum of CO, when they deduce 170 kcal./gm.-atom as the heat of sublimation into 4S atomic states of carbon².

According to the dissociation scheme given by Schmid and Gerö, the energy distance of the $X^1\Sigma$ ground state of CO from the $C(^4S) + O(^3P)$ atomic term combination is 11.06 eV. (with the original conversion factors), and this energy value is to be taken into account in thermochemical calculations involving tetravalent carbon compounds, or in determining the heat of sublimation of carbon. In CO, carbon is divalent, the ground-state dissociating accordingly into an atomic term combination corresponding to a carbon state of the s^2p^2 configuration, probably into $O(^3D) + O(^3D)$, the bond energy of CO ($X^1\Sigma$) being in this case 10.1 eV., while for the energy distance of the CO ground-state from the lowest $C(^3P) + O(^3P)$ atomic term combination gives 6.89 eV. Unfortunately, these results have often been misunderstood, in calculating the heat of sublimation of carbon from this last dissociation energy value, whereas the heat of sublimation of carbon is connected with the value corresponding to carbon atoms in the 4S state. The spectroscopic value 170 kcal. is in excellent agreement with the dynamic sublimation heat value resulting from the rate of loss in weight of heated carbon filaments, while the lower value resulting from an equilibrium measurement in the carbon arc can be interpreted by a statistical equilibrium between C atoms and C_2 molecules³.

Meanwhile, several authors have arrived at the conclusion that the heat of sublimation of carbon should be 170 kcal. Thermochemical considerations of White⁴, the reconciliation of some kinetic and thermochemical data by Baughan⁵, the conclusions of Kynch and Penney⁶ from absorption bands of mesomeric hydrocarbons, and the recent note of Sidgwick and Springall⁷ concerning the Hg-C bond all point in this direction. According to the interpretation of Schmid and Gerö, the corresponding conclusions can be maintained or suitably re-interpreted in taking into account that the organic compounds dealt with are built up from tetravalent 4S atoms, and the bond energies are to be calculated from an energy value corresponding to the 4S term of carbon.

Against the dissociation scheme of CO given by Schmid and Gerö, Herzberg puts first of all a theoretical argument the non-crossing of the energy curves of the two-centre problem, and applies this argument also to the sublimation of carbon in deducing the formation of 4P carbon atoms⁸. But as can be shown⁹, the conclusions resulting with respect to the energy curves of the two-centre model cannot be transferred to the potential curves of the vibrating and rotating molecule, the electronic motion (the averaging with respect to which of the interactions between all the particles leads to the potential curve determining the motion of the nuclei) also being influenced through the interaction by the motion of the nuclei. The co-ordination of Schmid and Gerö is supported by a large number of arguments in their paper, among the more recent results being an observed pre-dissociation limit at 8.83 eV.¹⁰, and the convergence of the $P^1\Sigma$ state to 10.1 eV.¹¹. According to still unpublished calculations of Gerö, the resulting value of the heat of sublimation of carbon can give a satisfactory account of a great variety of thermochemical data of organic compounds.

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WHILE agreeing with our emphasis of the significance of the 4S state of carbon for the calculation of bond energies in its compounds, Valatin, from an analysis of the CO spectrum proposed by Schmid and Gerö, implies alternative numerical values to the quantities which we have termed L_1 and L_2 , and for which we have proposed the values 125 and ~ 190 kcal./gm.-atom respectively. The scheme quoted by Valatin would mean in effect that $L_1 = \sim 73$ kcal. and $L_2 = 170$ kcal., values which are in serious conflict with other relevant data. It should be emphasized that, since more than one interpretation may be devised for the CO spectrum, spectroscopic arguments alone lead to no conclusive value for $D(\text{CO})$ and hence L_1 . Only a consideration of the spectroscopic data with all the evidence available from other sources will allow a final selection to be made.

Direct or indirect measurements of the vapour pressure of graphite by both the equilibrium and dynamic methods have, in the past, led to varying results for the heat of sublimation, some as high as 200 kcal. or more. In general, the determination of the vapour pressure under equilibrium conditions provides considerably lower figures for the heat of sublimation than does the dynamic method; and the equilibrium method alone (after a statistical allowance for the pressure of C_2 molecules has been made) is capable of providing a direct measure of L_1 . Whereas some determinations, in particular the approximate equilibrium measurements of Thiel and Ritter² and Basset³, have indicated values for L_1 so low as about 125 kcal., none has provided values appreciably lower than this figure. For conditions under which true equilibria have been established, equilibrium concentrations of both free carbon atoms in their ground (4P) state and C_2 molecules

must be considered, and we do not regard as justifiable Schmid and Gerö's effectual neglect of the 4P atomic state in carbon vapour⁴ in their discussion on the results furnished by the equilibrium method. The precise value of $D(C_2)$ is unfortunately not settled: whereas one estimate places it so low as 83 kcal./mol., it may be so high as 150 kcal., but could scarcely be appreciably higher than this figure.

The theoretical total vapour pressure values for carbon with the intermediate assignment $D(C_2) = 125$ kcal. have been calculated by Goldfinger and Jeunehomme⁵. The highest reasonable assumption regarding $D(C_2)$ could not reconcile the observed pressures with a value of L_1 much below 125 kcal., and since these authors further demonstrate that even $L_1 = 107$ kcal. necessitates a vapour pressure much too high to be a likely value, it is still more difficult to accept the much lower value (~ 73 kcal.) implied by Schmid and Gerö's analysis, which requires vapour pressures several powers of ten greater than have ever been observed. Furthermore, the low value 6.9 eV. for $D(\text{CO})$, from which this figure is derived, finds no place in the empirical relationship for similar diatomic molecules observed by Barrow⁶, which necessitates a dissociation energy for CO in the neighbourhood of 9 eV.

From the point of view of bond energies, L_2 is by far the more interesting quantity. Theoretical considerations⁷ have led to the expectation that the mean bond energy in the methyl radical is slightly greater than in methane. From the heat of formation of methane, the dissociation energy of H_2 , and the energy required to remove a hydrogen atom from the methane molecule⁸, it can be shown that the mean bond energy in CH_3 will exceed that in CH_4 only if $L_2 > 182$ kcal. This, and other considerations regarding the relative energies of reorganisation of methyl and ethyl radicals on their formation from methane and ethane respectively, lead us to ~ 190 kcal. for L_2 . This figure is also to be preferred from the calculation of the heat of sublimation (177 kcal.) by the dynamic method⁹, since it would follow from the arguments of Herzberg¹⁰ that this method provides only a lower limit for L_2 .

That the inferred figure, ~ 65 kcal., for the difference between L_2 and L_1 , that is, the excitation energy of 4S carbon, is to be preferred to the value ~ 97 kcal. (favoured by Schmid and Gerö) is strongly indicated by three independent lines of thermochemical evidence which are discussed at length in our forthcoming paper¹¹. These include experimental data regarding the stability of the formyl radical, which place an upper limit of about 75 kcal. on the C: 4S excitation energy. In accord with this, a calculation by Ufford¹² places this excitation energy at ~ 73 kcal.

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A 'New' Human Blood Group Antigen of Frequent Occurrence

THE sera of two women, whose babies were suspected of suffering from haemolytic disease of the newborn, were recently found to contain identical agglutinins of a variety not previously described. The serological examination of the two families is at present incomplete, but there is so far no definite evidence in either case that the agglutinin concerned is the result of immunization of the mother by the fetus. Indeed, the red cells of one of the jaundiced babies were not agglutinated by its mother's serum: this points towards the agglutinin being spontaneous rather than immune.

The antibodies are active at 37°C.; they appear slightly stronger at room temperature: at 10° their effects are masked in both cases by strong non-specific cold agglutinins. Both the women are of group O and the α - and β -agglutinins are difficult to absorb from the sera without diluting out or removing most of the 'new' agglutinin. Hence nearly all examinations have been carried out on group O red cells.

Out of 96 group O bloods of English people, mostly unselected but some selected for their Rh type, 24 (or 25 per cent) are agglutinated. Reactions are mostly well-defined positive and negative: one doubtful result has been eliminated from this count, and it is possible in view of the weakness of the antibodies that some positives have been missed.

The 'new' agglutinin has been shown to be independent serologically of the ABO, MN, Rh, P and Lutheran systems. It is also independent of the 'Kell' system, which was shown to be responsible for a case of haemolytic disease of the newborn—case No. 14 of Coombs, Mourant and Race¹. By kind permission of Mrs. H. D. G. Lewis, who has the 'new' antibody, and of her husband, the name 'Lewis' is proposed for the antigen.

Fifteen families have been studied from the point of view of the inheritance of the agglutinin. In seven cases both parents of a Lewis-positive person have been examined. In every case at least one of them is also positive. This is conclusive evidence that the agglutinin is inherited, and suggestive, but not statistically significant, evidence that it is a Mendelian dominant character rather than a recessive. No evidence has yet been found of genetic linkage with other blood group antigens.