

THE HEAT OF FORMATION AND STRUCTURE OF THE CARBON-OXYGEN AND CARBON-SULPHUR LINKAGES.

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The heat of linkage in diatomic molecules can be determined directly and the process of dissociation followed in detail. In the case of polyatomic molecules our knowledge of the dissociation process is not so complete. Although the dissociation has been determined spectroscopically in some cases, the heats of linkage in polyatomic molecules are usually evaluated from the thermochemical heat of formation of the molecule from its elements. This method depends on the assumption that the heat of any linkage is independent of the other linkages in the molecule, and has led to consistent values for the energies of many links. This assumption however cannot be generally true, as will be shown later. In the present work the energy of the CS and hence the CO linkage in carbonyl sulphide has been determined by photo-chemical methods and the absolute energy values of these linkages have been calculated. These values have been compared with those of the CS and CO bonds in similarly formed molecules and some conclusions with respect to the valency of the carbon atom and the structure of these molecules have been drawn. The relationship of the force constant to the type of the linkage has been discussed in detail for a number of molecules.

Experimental.

Carbonyl sulphide was prepared by dropping a concentrated solution of potassium thiocyanate on to sulphuric acid (290 c.c. in 400 c.c. water). The gas contained about 2 per cent. carbon dioxide and small quantities of carbon disulphide, hydrogen sulphide and possibly hydrogen cyanide. It was purified by passing through 33 per cent. caustic potash and the carbon disulphide removed by adsorption with freshly ignited wood charcoal. The gas was dried with phosphoric oxide and was stored over mercury and mercuric oxide for several days before use, in order to remove the last traces of hydrogen sulphide and hydrogen cyanide. Without careful purification the absorption spectrum showed faint traces of a banded structure, but with the pure gas this disappeared.

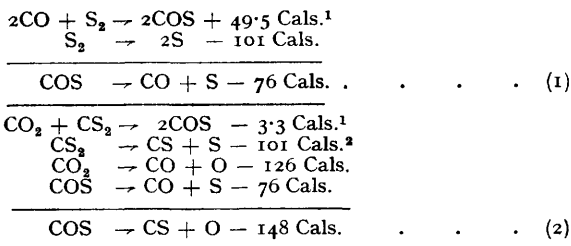
The absorption cell was a glass tube 4 cm. in diameter and 1 metre in length, with ground quartz windows. The system for evacuation consisted of a two-stage mercury vapour pump and oil pump, the pressure in the tube being measured by a mercury manometer. The spectrum was photographed with a quartz spectograph giving a dispersion of 12.5 Å./mm. at 2500 Å. A water-cooled hydrogen discharge tube was used as a source of light and a copper spark employed as a comparison scale.

Results and Discussion.

The spectrum of the pure gas showed a complete transparency to 2550 Å., at which point a strong continuous absorption appeared starting

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from a sharp edge and extending towards the violet. The absorption limit for a series of pressures was determined graphically from direct photometric measurements and found to be at $2550 \pm 20 \text{ \AA}$. The spectrum is interpreted as corresponding to the dissociation of the carbonyl sulphide molecule. The products of dissociation are CO and S or CS and O, one of which, in each case, may be in the excited state. The dissociation energies as calculated from thermochemical data are 76 and 148 Cals. respectively.



The determined photochemical dissociation energy is 4.84 volts or 111 ± 1 Cals. and hence the dissociation must proceed according to (1). This was also indicated by a deposition of sulphur on the walls of the absorption tube. The difference between the photochemical and the thermal value is the excitation energy of the carbon monoxide molecule or the sulphur atom. Since the lowest excitation potential of the carbon monoxide molecule is 5.9 volts above the ground level it is suggested that the sulphur atom is excited. The lowest possible excitation energy corresponds to the difference between the 3P ground level and the 1D metastable state. The position of the latter term has not hitherto been fixed from the S spectrum. By analogy with the oxygen atom (corresponding energy 1.96 volts) McLennan and Crawford³ suggested 1.2 volts for the position of this term. The latter value, however, may not be accurate as has been shown from general considerations by Frerichs.⁴ Christy and Naudé⁵ have recently determined the predissociation spectrum of sulphur and give a value of 1.6 volts for this energy difference. This is in satisfactory agreement with the above experimental value.

Heat of Linkage of the CO and CS Bond.

It is generally accepted that both carbon dioxide and carbon disulphide have a symmetrical linear structure. Recent investigations by Bailey and Cassie⁶ and Kohlrausch⁷ on the infra-red and Raman spectra of carbonyl sulphide indicate that this molecule is intermediate in its structure between carbon dioxide and carbon disulphide. A linear triatomic molecule XYX has three fundamental frequencies of vibration. Assuming that increased vibrational energy leads to dissociation of the molecule, it is clear that only the most unsymmetrical vibration ν_3 (or a combination of ν_2 and ν_3) can lead to XY and X as the products of dissociation. If dissociation followed from ν_1 and ν_2

¹ Stock, *Ber.* **57**, 719, 1924.

² Landolt-Börnstein Tabellen, vol. 5, 1019.

³ McLennan and Crawford, *Nature*, **124**, 874, 1929.

⁴ Frerichs, *Physic. Rev.*, **36**, 406, 1930.

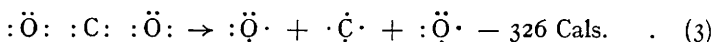
⁵ Christy and Naudé, *Physic. Rev.*, **37**, 907, 1931.

⁶ Bailey and Cassie, *P.R.S.*, **135 A**, 375, 1932.

⁷ Kohlrausch, *Physikal. Z.*, **33**, 165, 1932.

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directly the products would be $2X$ and Y . As an example of the latter type we may consider the ideal dissociation of carbon dioxide such that both oxygen atoms are removed simultaneously as in (3)



The products will be two normal oxygen atoms and a quadrivalent carbon atom (in the 5S metastable state). The thermochemical value for the complete dissociation into normal atoms is 363 Cals. This is greater than required in (3) by an amount equal to the excitation energy of carbon atom. This energy, the difference between the 3P state (ground state of the triplet system) and the 5S state (ground state of the quintet system) is about 1.6 volts or 37 Cals.

The energy required for the process (3) is therefore $363 - 37 = 326$ Cals. Since the carbon dioxide molecule is symmetrical, this gives a value of 163 Cals. for the true heat of linkage of the $C=O$ bond, which is in agreement with the energy of the $C=O$ bond in aldehydes and ketones (page).

Carrying out the same process with the carbon disulphide molecule, the corresponding values are 263 Cals. (heat of formation*) - 37 Cals. leaving 113 Cals. for each $C=S$ bond. The same values for the bond energies satisfy the carbonyl sulphide molecule. The energy of dissociation by a process similar to (3) is $310 - 37$ Cals. = 273 Cals., which is the sum of the absolute heats of linkage of the $C=O$ and $C=S$ bonds ($113 + 163$ Cals.).

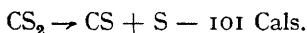
It must be emphasised that the complete dissociation in one stage, although the bonds in symmetrically formed molecules are equal, is essentially different from carrying out the dissociation in two steps. The splitting of the first bond requires a different energy according to the rearrangement of the electronic configuration in the remainder of the molecule. Thus the splitting of the first oxygen from the carbon dioxide molecule needs only 126 Cals., leaving 237 Cals. for the remaining CO bond. This is the same as the dissociation energy of the carbon monoxide molecule into normal atoms as determined from band spectra. It seems therefore that a valency rearrangement takes place after the removal of the first oxygen atom to give a triple bond between the carbon and the oxygen, as is normally assumed in the carbon monoxide molecule. On the other hand, although the structure of carbon monoxide is usually given as $C \equiv O$, the bond must still be attributed to a divalent carbon atom in the 3P state.† The third link, however, may be co-ordinate as indicated by dipole moment measurements.⁸ Furthermore, the same value for the $C \equiv O$ bond is obtained from the dissociation energy of the carbonyl sulphide molecule. The dissociation into carbon monoxide and a normal sulphur atom requires 76 Cals., leaving 237 Cals. for the $C \equiv O$ bond.

* The heats of formation of the CS_2 and COS molecules are taken from a paper by Bailey and Cassie, *Proc. Roy. Soc.*, **135 A**, 375, 1932.

† Mecke has suggested (*Leipziger Vorträge*, p. 37, 1931), that in the representation of the chemical bond the number of electrons contributed by each element should be shown. Thus he gives the formula of carbon monoxide as $C(4 + 2)O$, that is, the carbon contributes four electrons. This is not in agreement with the above view, and it seems necessary to write the formula $C(2 + 4)O$ since firstly, the products of dissociation are normal (not quadrivalent) carbon and oxygen; and secondly, the similarity between CO and N_2 shows that the oxygen provides the two electrons of the co-ordinate link.

⁸ Hammick, New, Sidgwick and Sutton, *J.C.S.*, 1876, 1930.

The corresponding value for the carbon disulphide molecule is



Since the total heat of formation is 263 Cals. the energy of the remaining CS linkage is 162 Cals. From band spectra analysis of the CS bands an upper limit to the dissociation energy of 192 Cals. is obtained. Closer agreement may not be expected since the linear extrapolation was carried out over a wide region. The same energy (162 Cals.) is obtained from the dissociation of the carbonyl sulphide molecule. The splitting of the oxygen atom requires 148 Cals., and thus the CS bond energy is $310 - 148 = 162$ Cals. By analogy with the $\text{C} \equiv \text{O}$ this corresponds to the energy of the $\text{C} \equiv \text{S}$. The heats of linkage are summarised in the following table.

TABLE I.

Bond.	Molecule.				Absolute Value.
	CO_2	COS.	CS_2	$\text{H}_2\text{CO.}$	
$\text{C}=\text{O}$	126	148	—	155	163 Cals.
$\text{C}=\text{S}$	—	76	101	—	113 Cals.

$\text{C} \equiv \text{O}$	237 Cals.	$\text{C}-\text{O}$	70.5 Cals.
$\text{C} \equiv \text{S}$	162 Cals.	$\text{C}-\text{S}$	58.7 Cals.

The energy of dissociation of the $\text{C}=\text{O}$ bond in formaldehyde as determined photochemically⁹ is 155 Cals.



The value is higher than that of the $\text{C}=\text{O}$ energy in carbon dioxide and carbonyl sulphide since the hydrogen atoms have very little influence on the vibration of the CO group. The dissociation energy would therefore be expected to approach the absolute value of the bond.

The last values in Table I. are the dissociation energies of the singly linked carbon-oxygen and carbon-sulphur bonds as found in dimethyl ether and dimethyl sulphide.¹⁰ Neglecting the influence of the hydrogen atoms the values of 71 and 59 Cals. respectively can be regarded as close approximations to the true link energies of the single bond. It follows therefore that the absolute energy value of the double link is approximately twice that of the single link and that of the triple bond three times that of the single link.*

Valency and Force Constants.

Up to recent times interest in the chemical valency bond has been directed mainly to a clear understanding of the structure and saturation of the bond. The question has continually arisen as to whether we can assign to each valency bond a definite bond strength. In this respect valuable contributions have been obtained by spectroscopic methods

⁹ Herzberg, *Trans. Far. Soc.*, **27**, 378, 1931.

¹⁰ Sidgwick and Bowen, *Annual Reports*, p. 401, 1931.

* A similar relationship has previously been found by Bailey and Cassie (*loc. cit.*)⁶ for the force constants.

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and numerous studies of the Raman effect have led to a simple classification of the various types of linkage which occur in molecules. These have been divided into two classes, (1) those links, the frequencies of which vary only slightly in different molecules, and (2) those whose frequencies are essentially dependent on the structure of the molecule, the so-called "inner" and "outer" vibrations respectively.¹¹ This classification, however, is quite arbitrary since the same type of linkage may in some compounds be an "inner" and in others an "outer" vibration. For example, the C=O group in all ketones gives rise to approximately the same frequency at 1700 cm.^{-1} , that is the group vibrates as a unit against the remainder of the molecule. On the other hand, in the carbon dioxide molecule the CO vibration is greatly influenced by the presence of the second oxygen. There is no longer a single CO vibration but the molecule vibrates as a whole involving two CO frequencies. In order to obtain some idea of the strength of binding of a given link it has been general to calculate the value of the force constant (restoring force per unit displacement) from the frequency of vibration.* This has led to the interesting result that the force constants of the frequencies of the inner vibrations of the lighter elements have approximately the same value for the same type of link, and the force constant of the double bond is twice and that of the triple bond three times as strong as the single bond. (Table II.).

TABLE II.

Bond.	Force Constant.	Bond.	Force Constant.	Bond.	Force Constant.
C—C	4.40	C—O	5.0	C—N	4.5
C=C	11.0	C=O	11.7	—	—
C≡C	16.4	C≡O	18.8	C≡N	19.2

Although these simple relationships have been of great value in determining the type of linkage, it should be pointed out that the application of this result is confined to the lighter elements of the first period of the periodic table. With the heavier elements, apart from their larger bond separation, it is necessary to consider the greater polarisabilities of the atoms. This brings about a marked change in the force constants of otherwise similar linkages. For example, the force constants of the halogen elements show a fourfold decrease from fluorine to iodine. Similar decreases are observed in other series of elements (Table III.). From a consideration of the above results it is apparent that the force constant has not a characteristic value for the single and double bond respectively.

¹¹ Kohlrausch, *Der Smekal-Raman Effect*, Berlin, 1931.

* Kohlrausch prefers to use the "mean restoring force," that is, the product of the force constant and the amplitude of vibration. However, the conclusions drawn in this paper regarding the force constants of molecules apply equally well to the "mean restoring force." On the other hand, Mecke characterises the bond by *Bindungswert*, i.e., the work required to double the atomic separation. These values are determined by the electronic configurations of the molecules, and have approximately the same values for corresponding molecules or compounds, for example the *bindungswert* for the halogens are F—F 36.6, Cl—Cl 40.4, Br—Br 40.9, I—I 37.8 volts. The value of the *Bindungswert* is not, however, a finite constant for the single, double or triple bond, but depends on the electron affinity of the constituents of the molecule.

TABLE III.

Molecule.	Force Constant.*	Molecule.	Force Constant.
	dynes/cm.		dynes/cm.
F—F	7.11×10^5	O = O	11.4×10^5
Cl—Cl	3.23 "	S = S	4.95 "
Br—Br	2.44 "	Se = Se	3.47 "
I—I	1.69 "	Te = Te	2.46 "

A similar variation of the force constant is found with many other atomic linkages of the same valency type. Some typical results are given in Table IV.

TABLE IV.

Molecule.	Force Constant.	Molecule.	Force Constant.
	dynes/cm.		dynes/cm.
C = O	14.2×10^5	C $\equiv$ O	18.8×10^5
C = S	6.9 "	Si $\equiv$ O †	9.1 "
S = O	7.74 "	—	—

Bailey and Cassie (*loc. cit.*)⁶ have concluded that the values of the force constants of the CS linkage indicate a single linkage between the carbon and the sulphur and that the formation of multiple bonds is confined to elements of the first period. This is not in agreement with the usual chemical conception of the sulphur double bond. The sulphur molecule appears to be similar to the oxygen molecule in every respect. The binding properties are identical, both molecules having a $^3\Sigma$ ground state indicating two unshared electrons. Furthermore, according to the theory of "binding" and "loosening" of electrons of Herzberg¹² the bond in each case is doubly linked. The observed decrease in the magnitude of the force constant of the C = S linkage compared with that of the C = O linkage can be explained by the decrease of the force constant for the double link from oxygen to tellurium as shown in Table IV.

Structure of Carbon Dioxide, Carbon Disulphide, and Carbonyl Sulphide Molecules.

In a recent paper on the analysis of the vibration types of simple molecules Mecke¹³ suggests that the CO bonds in carbon dioxide and carbon monoxide are similar in nature and assumes that the smaller energy necessary to split off the first oxygen atom from the carbon

* These values are directly comparable, since they refer (with the exception of fluorine) to the same electronic states of the molecule, *viz.*, $^1\Sigma$ ground state. The corresponding level for fluorine is accepted to be $^1\pi$, but this is doubtful, since no absorption measurements on this gas have been made. The force constants have been calculated from ω as obtained from band spectra data.

† The similarity of these molecules is evident from band spectra. The resonance transitions in both molecules are $^1\pi \rightarrow ^1\Sigma$ indicating similar electronic configurations (Saper, *Physic. Rev.*, **40**, 465, 1932).

¹² Herzberg, *Leipziger Vorträge*, 1931.

¹³ Mecke, *Z. physik. Chem.*, **16**, 409, 1932.

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dioxide molecule results from the polarisation forces of the second oxygen atom. Mecke neglects the excitation energy of the carbon atom, and gives a structure for carbon dioxide which involves two triple bonds. The electronic configuration of the carbon monoxide molecule is identical with that of the nitrogen molecule and contains a triple linkage, although the carbon atom is still in the divalent state (page). In the carbon dioxide molecule the carbon atom is at least quadrivalent and the possible structures are $\ddot{\text{O}}::\text{C}::\ddot{\text{O}}$ and $\text{:O}::\text{C}::\text{O:}$. In support of the latter, Mecke assumes that the dissociation of the carbon dioxide molecule gives an excited oxygen atom and a normal carbon monoxide molecule, and this is necessary to give him the correct energy balance. This does not occur since Herzberg¹⁴ has recently shown that the dissociation takes place by a process analogous to predissociation and gives normal atoms. The first structure seems the more likely and agrees with the values of the heats of linkage and the force constants of the bonds. In the same manner it is concluded that all the linkages in carbonyl sulphide and carbon disulphide are double bonds. This is supported by the recent work of Pauling¹⁵ in which it is shown that two double bonds must of necessity be at 180° to one another and that the structures $\text{O}=\text{C}-\text{S}$ and $\text{S}-\text{C}-\text{S}$ cannot be linear.

Summary.

The photochemical dissociation of carbonyl sulphide leads to a normal carbon monoxide molecule and an excited sulphur atom in the ^1D state (excitation energy 35 cal.).

The absolute values of the heats of formation of the $\text{C}=\text{O}$ and $\text{C}=\text{S}$ bonds in carbon dioxide and carbon disulphide have been calculated from the thermochemical heats of the ideal dissociation process, that is, complete dissociation in one stage. This process gives an excited carbon atom (^5P), whereas the dissociation in two stages gives a normal carbon atom (^3S). The wide variation in the heat of formation of the $\text{C}=\text{O}$ and $\text{C}=\text{S}$ bonds in different compounds is attributed to the influence of the neighbouring atoms on the normal vibrations. The $\text{C}=\text{O}$ bond energy in formaldehyde is approximately equal to the absolute value.

It is concluded that the value of the force constant is not a characteristic of the type of linkage, although this appears to be true for the elements of the first period. The force constants of corresponding linkages show a marked decrease with increasing atomic weight of the constituent elements.

The force constants and the heats of linkage of the CO and CS bonds in carbon dioxide, carbonyl sulphide and carbon disulphide show that all the bonds in these molecules are doubly linked.

In conclusion, the authors wish to express their thanks to Professor W. L. Bragg, F.R.S., for the kindness with which he placed every facility at our disposal, and to Mr. E. Eastwood for assistance with the experimental work of this paper.

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¹⁴ Herzberg, *Z. physik. Chem.*, **17**, 68, 1932.

¹⁵ Pauling, *J.A.C.S.*, **53**, 1367, 3225, 1931.