

AN ENERGETICAL INTERPRETATION OF THE SEMIPOLAR DOUBLE BOND.

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ABSORPTION spectra of inorganic nitrates in the vapour state have been investigated simultaneously by Butkow and Tschassowenny¹ and by Haq and Samuel² with almost identical experimental procedures and results. There is little doubt about the covalent nature of the metal-oxygen bond of these compounds in the vapour state, and the transition to electrovalency in solution, as pointed out elsewhere,³ is due to the additional energy of hydration.

There appears to be, however, a difference of opinion as to the character of the second $N = O$ bond of the nitro-group. Butkow and Tschassowenny interpret their results by means of the semi-polar double bond, introduced by Sidgwick a.o.,⁴ whereas we consider the same experimental results as a further argument against the existence of such co-ordinate linkages in simple inorganic molecules of first order. In the following we give therefore an energetical interpretation of this phenomenon based on a number of experiments on the photo-dissociation of inorganic molecules.⁵ It retains, we believe, the essential features of this conception as far as chemical reactivity is concerned, without introducing a second variety of covalency for such molecules.

In the case of the nitro-group some difficulties occur on account of the inaccuracy and the lack of certain thermochemical figures. Hence we begin with the exactly similar example of the sulphates and sulphites and consider first the formation of the SO_2 and SO_3 molecules. The bonds in SO and SO_2 are very nearly related to each other. The dissociation energy of SO taken from its band spectrum⁶ is 5.05 e.v., the atomic energy of formation* of SO_2 is 246.4 k.cal./mol. = 10.7 e.v. which is almost precisely double the former value. Furthermore, the analysis of the near ultra-violet SO_2 bands⁷ shows, that the energy of excitation and the symmetric valence vibration of the excited and unexcited state are almost identical with the corresponding

* The thermochemical figures and calculations are the same as in the preceding papers.^{5,7} Some figures are slightly changed on account of the data of K. K. Kelley's new survey on the "Free Energies of Vaporization and Vapour Pressures of Inorganic Substances" (Bureau of Mines, U. S. Dept. of the Interior, Washington, 1935).

values of the SO molecule. Moreover, a large number of investigations of the absorption spectra of halides and oxyhalides of S, Se and Te have shown that the energy of bonds such as S = O, S = S, Se = O, Se = Se, S - Cl, S - Br, Se - Cl, Se - Br, etc., remain almost unchanged in such widely different molecules as SO, SOCl₂, SOBr₂, S₂, SCl₂, S₂Cl₂, SeO, Se₂, SeO₂, SeOCl₂, Se₂Cl₂, SeCl₄, etc.

In all these molecules the central atom is in the di- or tetravalent state. For molecules such as SO₃, SO₂Cl₂, etc., involving hexavalency of the central atom, the law of approximate additivity of the bond energies at the first glance appears not to hold good. The atomic energy of formations of SO₃ is 325·6 k.cal./mol. = 14·1 e.v. which is distinctly lower than three times D (SO) and in other cases, *e.g.*, PCl₃ and PCl₅, etc., the disagreement is even much larger.

The explanation is quite simple. The formation of SO₃ is not brought about by the combination of unexcited SO₂ in its ground state $^1\Sigma$ plus unexcited oxygen atoms in the 3P term. The electronic configuration of the sulphur atom is $3s^23p^4$ and its di- and tetravalent state involve unexcited sulphur atoms. To make sulphur hexavalent an excitation to a $3s3p^5$ term is indispensable because the completed group $3s^2$ does not possess bonding power, but acts repulsively only.† This view of the Heitler-London pair bond theory of valency has been supported by direct spectroscopical evidence.⁸ The ground level of SO₃ therefore does not belong to the same series as those of the SO and SO₂ molecules. The normal states of these later compounds are formed by combination of unexcited atoms and molecules, whereas the adiabatic dissociation of unexcited SO₃ involves excited products. Experimentally this is quite certain, as both molecules SO₂ and SO₃ are diamagnetic, which a molecule formed by the combination of SO₂ ($^1\Sigma$) plus O (3P) could not be. All spin vectors being counterbalanced already in the singlet level of SO₂, there are no free vectors left to neutralise those of the triplet term of oxygen to yield a singlet term of SO₃.

The relative position of the ground states of the three molecules is shown in the simplified Franck-Condon Diagram of Fig. 1 of the system S + 3O. The approach of unexcited O atoms towards the unexcited S atom or the unexcited SO molecule leads to the formation of SO and SO₂ molecules. But on the approach of unexcited O atoms towards unexcited SO₂ no chemical union but an elastic collision takes place. This is represented in

† A more detailed discussion on the electronic configurations of the atoms and their valencies in polyatomic molecules will be found in a forthcoming paper by Lessheim and Samuel.

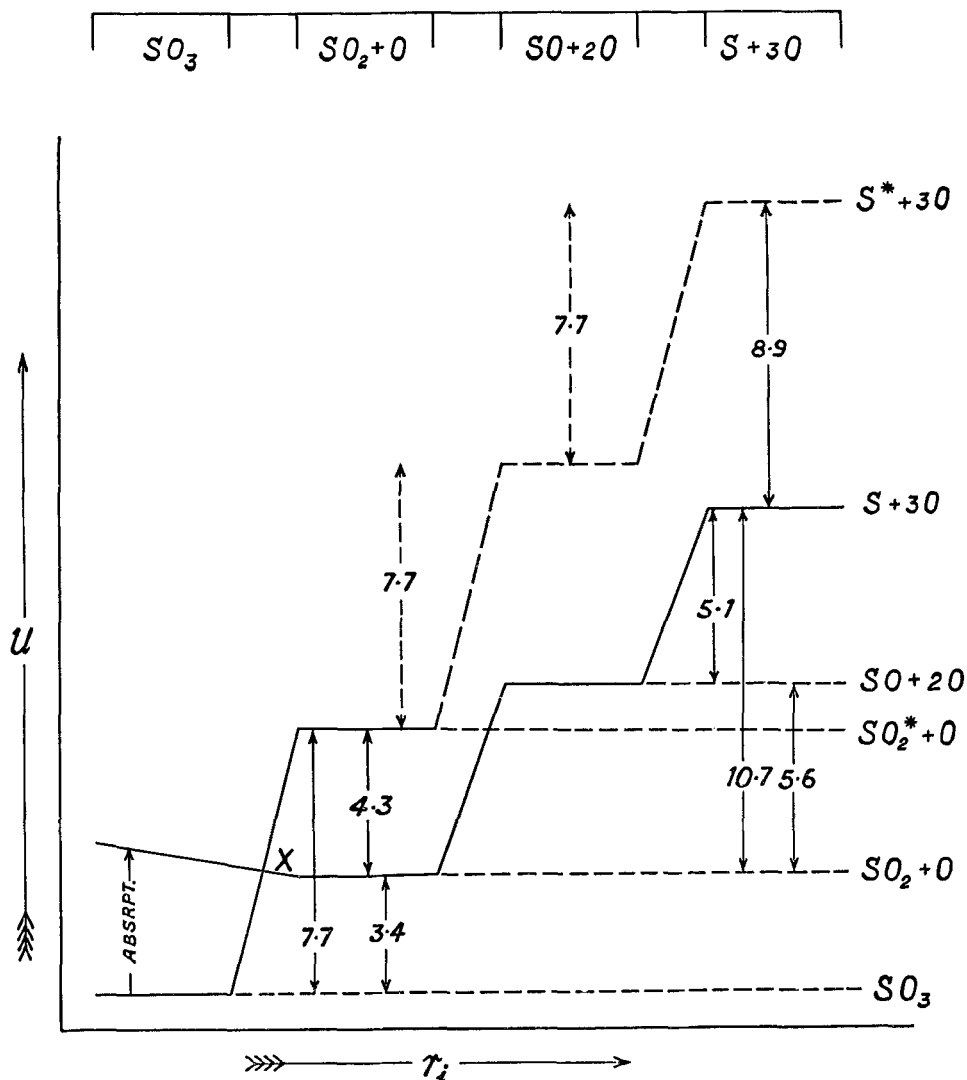


FIG. 1.

the diagram by a repulsive curve without a stable minimum. The products of adiabatic dissociation of SO_3 most certainly are either $\text{SO}_2 + \text{O}^*$ or $\text{SO}_2^* + \text{O}$ plus O and no direct experimental evidence exists at present which permits to decide between these two possibilities. Theoretically, however, chemical union is not possible unless the original s^3 group is split previously. Therefore in the diagram the ground level of SO_3 is connected with a level involving an excited SO_2 molecule. The energetic position of this level can be estimated. The adiabatic dissociation of this state finally involves a sulphur

atom in the $3s3p^5$ configuration. The known state $3s3p^5\ ^3P$ appears to be identical with the lowest term of this configuration. It has an energy of excitation of 8.9 e.v. which added to $D(\text{SO}_3) = 14.1$ e.v. yields a value of 23.0 e.v. for the adiabatic energy of dissociation of SO_3 into $\text{S}^* + 3\text{O}$. For the mean bond energy $D_B(\text{S}^{\text{vi}} = \text{O})$ taken as one-third of this figure, 7.7 e.v. obtains. The term of excited SO_2 therefore lies approximately 7.7 e.v. above the ground level of SO_3 or 4.3 e.v. above that of SO_2 .

The existence of the repulsive potential curve $\text{SO}_2(^1\Sigma) + \text{O}(^3P)$ is indicated by the absorption spectrum. The long wave limit of continuous absorption has been measured by various authors⁹ and lies at an energy value of about 80 to 85 k.cal./mol., slight differences being accounted for by the experimental difficulty to determine the value associated with the lowest state of vibration. This result therefore agrees very well with the energy difference $D(\text{SO}_3) - D(\text{SO}_2) = 81.2$ k.cal./mol. Kornfeld directly used the SO_2 absorption bands as an indicator of the photo-dissociation of SO_3 . Moreover, Dutta found the beginning of the second region of selective absorption at 124 k.cal./mol. The difference between the two long wave limits agrees with the excitation energy of the 1D term of $\text{O} = 1.96$ e.v. = 45.1 k.cal./mol.† Similarly, the long wave limit of the continuous absorption spectrum of TeO_3 lies at 62.1 k.cal./mol.¹⁰ and agrees with the thermochemical energy difference $D(\text{TeO}_3) - D(\text{TeO}_2) \sim 53$ k.cal./mol. Again that of SO_2Cl_2 at 108.6 k.cal./mol. agrees with the value $D(\text{SO}_2\text{Cl}_2) - D(\text{SOCl}_2) = 110.0$ and pyrosulphuryl chloride $\text{S}_2\text{O}_5\text{Cl}_2$ shows a long wave limit of almost the same value, *i.e.*, 113 k.cal./mol.⁵

For molecules of a *lower* state of valency of the central atom of the types PCl_3 , SCl_2 , SeCl_4 the first red wave limit always agrees with the bond energy and the products of photo-dissociation are unexcited atoms and radicals possessing free valencies.^{5,11} But the photolytic dissociation of such simple molecules formed by atoms in their state of *maximal* valency produces not radicals, but unexcited atoms and saturated molecules of lesser valency of the central atom; the red wave limit always agrees with the thermochemical difference of the atomic energies of formation of these two molecules. Just this difference of behaviour clearly indicates that in a molecule formed by hexavalent sulphur such as SO_3 the absorption of light corresponds to a transition from the ground level of the molecule to the repulsive

† Some difficulties experienced in the interpretation of the absorption spectra of SO_3 , etc., disappear on the replacement of the value of $D(\text{S}_2) = 4.4$ e.v. taken from predissociation data, by the new value of 3.8 e.v. calculated directly from the convergence point. (R. K. Asundi and R. Samuel, *Proc. Phys. Soc. Lond.*, 1936, **48**, 28; *Proc. Ind. Acad. Sci.*, 1936, **3**, 466.)

curve SO_2 ($^1\Sigma$) plus O (^3P), while an attractive curve involving these products does not exist.

The position of the binding level $\text{SO}_2^* + \text{O}$ 4.3 e.v. above the ground level of SO_2 is interesting also from another point of view. The origin of the near ultra-violet absorption bands has been located at $33303 \text{ cm.}^{-1} = 4.1 \text{ e.v.}$ ⁷ The appearance of the bands and the vibrational frequencies obtained make it difficult to identify the upper level of these bands with that term in which the s^2 orbital has been fissured. But Franck, Spomer and Teller¹² have shown that the pseudo-predissociation of these bands is due to perturbations owing to the existence of another electronic level in the immediate vicinity of the first one. The close agreement of the above figures derived in an entirely different way makes it probable that this disturbing term is indeed the excited level of SO_2 involved in the adiabatic dissociation of SO_3 .

These considerations may be summed up as follows :—

The energy difference (3.4 e.v.) between the ground level of a molecule whose central atom exhibits its maximal valency (SO_3) and the corresponding molecule of lesser valency of the central atom (SO_2) is less than the bond energy of the latter (5.4 e.v.) and much less than that of the former (7.7 e.v.). For chemical reactions, however, not the bond energies but their actual differences are decisive. For all practical purposes the oxidation of SO_2 may be described in the following way :—On the approach of unexcited oxygen atoms to unexcited SO_2 molecules the system will follow the repulsive curve with a small amount of energy of activation until the point of intersection (X in the diagram) with the potential curve of the ground level of SO_3 is gained. The thermochemical difference $D_T = D(\text{SO}_3) - D(\text{SO}_2)$ remains as chemical heat of reaction, whether the D values directly represent the sum of the bond energies or not.

Exactly the same conditions prevail in the corresponding molecules formed by nitrogen, but the calculation of the two bond energies is more difficult and uncertain. It is not permitted to divide, *e.g.*, the atomic heat of formation of N_2O_3 into three equal parts, two of the oxygen atoms being linked by double bonds, one by two single bonds. In the following table the atomic energies of formation D are listed together with the heats of formation Q from which they are derived§ :—

§ With $D(\text{N}_2) = 169.5$, $D(\text{O}_2) = 116.4$ and $D(\text{H}_2) = 102.7$. Q (HNO_2) refers to an aqueous solution, D (HNO_2) will be slightly smaller. Q (N_2O_3) is an older value (*cf.* Mellor, *Comprehensive Treatise*) and possibly not quite accurate.

	NO	NO ₂	N ₂ O ₃	N ₂ O ₅	HNO ₂	HNO ₃	NCl ₃	NOCl
Q	-21.6	-8.1	-22	-1.2	(30.8)	34.4	-54.7	-6
D	120.3	193.0	322.1	459.3	<282.3	345.1	117.8	126.9
D _T	73.3		2 × 68.6		> 62.8			

The differences D_T of the D values of corresponding molecules formed by tri- and pentavalent nitrogen respectively are about 70 k.cal./mol. and 69 k.cal./mol. have been deduced similarly² for ethyl nitrate and ethyl nitrite from their respective heats of combustion. The chemical heat of reaction of the oxidation of the nitroso group will be $D_T = 70$ k.cal./mol. Deducting $1/3D(NCl_3)$ from $D(NOCl)$ a value of 126.9 k.cal./mol. obtains for the bond energy $D_B(N^{III} = O)$ which is quite near to $D(NO)$. Adding the energy of excitation of $N(2s^2 2p^4 4P) = 250.7$ to $D(NO_2)$, 221.9 obtains for $D_B(N^V = O)$. Again the true bond energy, *i.e.*, the energy of adiabatic dissociation, of the state of maximal valency is larger than that of lower valency, whereas the heat of reaction D_T involved in the transition from one to the other is smaller than both.

The conception of the semi-polar double bond as a second kind of covalent linkage has been introduced for various reasons. Leaving aside genuine complex salts¹⁵ and speaking of molecules of first order only, these reasons may be conveniently divided into two classes. One series of arguments has been connected with the Octet Rule. It maintains that the formation of an electron octet confers stability to a molecule. Other arguments are mainly concerned with questions of stability and reactivity.

Considerations of the first kind have been discussed of late from the present point of view in a number of preceding publications.⁸ A few words may be sufficient here. The conception of the co-ordinate bond has been introduced in order to obtain a formal formation of an electron octet also in such cases where the central atom exhibits more than four valencies. The nitro-group is a typical example. It has been shown that this conception is contradicted by new band spectroscopical evidence which shows that just the so-called "lone pair" of electrons, the agent of co-ordination, is the completed s^2 group which does not possess bonding power. Furthermore, there does not exist any physico-chemical evidence which proves the existence of a second kind of covalent linkage in molecules of first order.

The covalency exhibited by the nitrates in the vapour state is also worthy of note. It may be recalled that the prevailing influence of octet formation was made apparent by two entirely different classes of molecules, the organic molecules, where it is the outcome of the tetravalency of C, and the simple salts which dissociate in solution into two ions possessing the configuration of the corresponding rare gas. As to the latter ones, the existence as free ions, *i.e.*, the existence of a positive electron affinity of negative ions mainly of group VII, and a low ionisation potential of the metals mainly of groups I and II, is of course due to their neighbourhood to the rare gases in the periodic table and the ease by which they assume their electronic configuration. But the number of valencies exhibited by such atoms is in no way connected with this phenomenon. Under suitable experimental conditions these electrovalent links may turn into ordinary covalent bonds, as has been shown by Franck and his collaborators¹³ in the case of silver halides and by Butkow, Oeser and Wieland¹⁴ in that of divalent metals with high ionisation potentials. The absorption spectra of the nitrates and sulphates in the vapour state show that even metals with very low ionisation potentials like Na or K, form covalent molecules if the electron affinity of the partner is sufficiently low. But atoms like K or Mg cannot be assumed to be surrounded by an electron octet in such molecules. Clearly the number of valencies exhibited is quite independent of the possibilities of octet formation and the electrovalent or covalent nature of the bond. As a matter of fact, just these experiments indicate again that numerical valency depends entirely on the number of outside electrons of an atom. It is therefore a property of the free atom quite independent of the partner. The existence of *e.g.*, the five, six, and seven covalent bonds of nitrogen, sulphur and iodine respectively does not constitute a new phenomenon; they do not require any other explanation than the covalent bonds of liquid LiEt or of AgCl vapour, etc., where likewise octet formation does not take place.

The second main argument for the introduction of a co-ordinate bond into the formulæ of such molecules of first order is of an energetical nature. In certain cases the transition from a lower to the maximal state of valency at first sight appears to produce bonds of less stability. A typical example is the reaction $\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2$ which indeed takes place with great ease and appears to indicate a reduced energy of the bonds of the last two chlorine atoms. Other examples are for group IV atoms, *e.g.*, the decomposition of PbCl_4 or SnCl_4 into PbCl_2 or SnCl_2 and for group VI the greater

stability of SO_2 as compared with SO_3 .[§] In all these examples the central atom of the less stable molecule exhibits its maximal valency according to the number of its outside $s + p$ electrons whereas the numerical valency of the central atom of the more stable molecules agrees with the number of the p electrons alone.

As has been seen, the true bond energies in such cases of maximal valency, as *e.g.*, PCl_5 , are rather increased, because the adiabatic dissociation of such a molecule involves an excited P atom, the s^2 group of electrons being split. The high reactivity is due to the low value of $D_T = D(\text{PCl}_5) - D(\text{PCl}_3)$ brought about by the beginning at an excited level of the adiabatic formation of the molecule. This places the ground level of PCl_5 at a level lower than that of PCl_3 but not as low as it would be otherwise. The corresponding figures are 3.4 and 5.4 e.v. for SO_3 and SO_2 respectively, but only the latter value represents a true bond energy.

The increased reactivity and the ease of such reactions, to our mind, are not an indication of a second variety of covalent linkage, *i.e.*, of a bond of lesser energy. They are brought about by the lack of free valencies of the molecules of lesser numerical valency. Further chemical combination takes place only after an excitation of this molecule involving a splitting of the original s^2 group of the central atom. An increased energy of adiabatic dissociation results always, but in certain cases the energy difference of the ground levels of the two molecules is considerably decreased and if the bond energies are not very great (as probably in SF_6) an increased reactivity results. Essentially, this is due to the non-bonding and repulsive character of the s^2 group in accordance with the Heitler-London pair bond theory of valency.

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[§] SO is again less stable in the chemical sense but on account of the two free valencies exhibited in its $^3\Sigma$ ground state.

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