Classical and Quantal Contributions to the Mechanisms of Ion–Molecule Reactions

Chemistry of O_2^+

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A semi-classical qualitative model is developed to predict the nature of collision complexes for thermal reactions of O_2^+ with neutral substrates. The initial geometry of this complex is assumed to be determined by the classical potentials of the system. Only the frontier orbitals of the two species which can overlap in this classical orientation then need to be considered in the rationalization of the *initial* progress of the chemical reaction. The model is further simplified by the use of the united atom model to characterize the frontier orbitals of the reacting species. It also leads to an analogy between O_2^+ and *d* block transition metal ions. The abundant data on the geometry and bonding of the substrates of interest with metal ions can then be directly compared to the nature of the gas phase complexes of O_2^+. In one case the geometry predicted in this way has been observed from a previous semi-empirical m.o. calculation. The model is applied qualitatively in the interpretation of the kinetics of gas-phase reactions involving O_2^+ and O_2, N_2, NO, NH_3, H_2O, CH_4 and N at 300 K.

Substantial data concerning the thermalized gas phase reaction of O_2^+ have been obtained from flowing afterglow studies.[1] There are three main types of reaction observed, electron exchange, atom exchange and complex formation. The amount of available information makes it possible to qualitatively interpret the kinetics of reactions involving O_2^+ with simple neutral molecules in terms of their electronic structures.

The kinetics of ion-molecule reactions have been extensively analysed in both the classical and quantum mechanical models.[1-3] Some semi-classical models have also been used in which the nuclear motions are treated classically and the electron rearrangements by quantum calculations.[4,5] This simplifies the manipulations somewhat at the cost of validity of the model. Thorson and Delos[5] have recently shown, however, that the classical equations of motion are valid to very low collision energies in spite of the fact that the reaction cannot be physically viewed as a collision between classical particles in the sense of the correspondence principle.

Some attempts have been made to characterize the microscopic nature of the " bound states " observed in collision experiments.[6-9] Classically these states are associated with capture of the moving particle if it passes within the impact parameter *p* of the target body. It is then forced to orbit around the target until it gains sufficient angular momentum to break free. Semi-classically, a more refined model may be developed. Assuming that the motions of the nuclei may still be described by classical equations, but that electrons are quantal, the existence of a bound state can be attributed to a classical orbiting phenomenon with the possible addition of a quantum mechanical stabilization of the collision complex arising from overlap of valence orbitals on the two colliding bodies.

The evaluation of both energies requires knowledge of the angular shape and radial extent of the attractive and repulsive potentials. In ion-molecule collisions, the classical potential energy is strongly orientation dependent and may be written;[1]

$$V(\mathrm{r}) = (-eD/r^2)P(\cos\theta)-(e^2/r^4)(\alpha_{||}-\alpha_{\perp})P(\cos\theta)-(e^2/r^4)[(\alpha_{||}+2\alpha_{\perp})/3] \quad (1)$$

in which D is the permanent dipole moment of the neutral molecule, $\alpha_{||}$ and $\alpha_{\perp}$ are the polarizabilities of the neutral molecule and r is the ion-molecule separation. Since these orientation dependent terms decrease more slowly than the spherical terms, they tend to dominate the scattering behaviour of thermalized systems. The classical behaviour of thermalized ion-molecule collisions has been examined by Dugan and co-workers [6] for several cases. With reasonable values of D, $\alpha_{||}$ and $\alpha,_{\perp}$ the torque experienced by the dipolar molecule is sufficient to cause alignment of the dipole in the field of the ion at a separation of 25 Å. At the classical turning point for the collision, this aligning torque varies characteristically from 2 eV for homonuclear diatomics to 5 eV or more for heteropolar molecules. The angular momentum of the whole system is conserved by being largely transferred to precession of the dipole about the aligning field or rotation of the whole complex, the latter corresponding to orbiting in systems of scalar potentials.

This locked-in geometry can be expected to strongly influence the decay of the complex into product channels. The only important routes for electron movement would be through orbitals of the collision complex which are allowed to overlap in the preferred geometry. If initially the orbitals of the two bodies correlate adiabatically during the collision,[7] then the identity of the one-electron valence orbitals of the collision complex and its possible states are readily established by the Wigner–Witmer rules.[8] If the collisions are at the low energy limit and the molecular core electrons may be ignored, approximate values of any possible quantal contributions to the stability of the bound state may be derived.

The analysis of the gas phase reactions of O_2^+ will be based on this model. The geometry and stability of the collision complex are assumed to be principally determined by the classical torque and attraction between the ion and dipolar molecule. Additional quantal stability may be gained *at short range* if valence orbital overlap is permitted by the classically established geometry.

If a favourable orbital overlap is achieved then an allowed chemical reaction will appear to have little or no activation energy. If the overlap required for reaction demands geometry different from that established, then the activation energy will correspond approximately to the torque necessary to achieve that required stereochemistry at the classical turning separation of the collision. Such an assumption would account for a substantial part of the activation energy observed [7] in the reaction of H_2 with CO^+. If on the other hand a favourable geometry is achieved but additional overlap or a curve crossing are necessary for reaction, then the activation energy would correspond to the additional collision energy necessary over that achieved by the action of the thermal and long range attractive forces. Such an assumption is essentially the same as the argument advanced by Schaefer and Henis.[9] The transition of a system from a reactant to product channel even though allowed both thermodynamically and by geometry, may be a very unfavourable process. This is the case when large rearrangements of electron density are necessary and such rearrangements most often involve the core or bonding electrons of the molecule. These electrons generally occupy strongly held, compact orbitals which cannot achieve significant overlap with the valence orbitals of a second body at low collision energies.

THE NATURE OF REACTING ORBITALS

The *initial* progress of chemical reactions in this approximation is viewed as being controlled by the Lewis basicity or acidity of the " frontier " orbitals [10] on the two reagents. If only moderate overlap is achieved at the classical turning point then this simple perturbation theory, as used in the kinetics of *d* block metal ions,[11] is very informative. If, as is unlikely at thermal energies, the turning distance is very short, more complicated curve crossings may occur requiring calculations involving configuration interaction.

The use of this simple model requires well characterized eigenfunctions of the frontier orbitals. These orbitals are usually the most delocalized valence levels of the molecule and the most difficult to calculate [12] with conventional LCAO techniques. Recently an important source of difficulty was identified from a comparison of CNDO and united atom (UA) models [12] for small molecules. Totally symmetric valence orbitals are characteristically destabilized because of a build-up of quantal interference charge density between atomic nuclei which cannot be stabilized by the available nuclear potential. This effect, termed the anisotropic potential destabilization (APD),[13] contributes strongly to the donor ability of such orbitals. Indeed the extent of destabilization is a much more reliable criterion of the Lewis basicity of an orbital than is its ionization potential. These basicities or the acidities of empty orbitals are more clearly identifiable in a UA correlation diagram of the molecular orbitals than in the LCAO model. For this reason, the molecular electronic structures of O_2^+ and some typical neutral molecules with which it may react are given in fig. 1. The construction of these and other relevant diagrams has been described elsewhere.[13] For each of the molecules discussed here ; O_2^+,[14] NH_3,[13] H_2O,[13] N_2,[14, 15] O_2 [14c, 16] and NO [15, 17] there is sufficient spectroscopic evidence both from u.v. and photoelectron spectroscopy to clearly characterize the symmetries and eigenvalues of the frontier orbitals.

To maintain $D_{\alpha h}$ symmetry, the UAMO diagram of O_2^+ has been constructed assuming a dissociation to the artificial limit of two $O^{\frac{1}{2}+}$ atoms. The orbital eigenvalues at the separated limit are obtained by interpolation between the electron affinity and first ionization potential of the oxygen atom, allowing for the half filled shell effect.[18] The ground configuration of O_2^+ correlates to the excited $3p^2 3d^1$ configuration of sulphur since the equilibrium internuclear distance is achieved before the $3d\pi_g$; $3p\pi_u$ curve crossing is realized (fig. 1(*a*)). Because of this symmetry required upward correlation of the highest occupied orbital, the frontier electron of O_2^+ is strongly antibonding in nature. In spite of its high ionization potential the O_2^+ ion in its ground state can act as a Lewis π base towards empty orbitals on a substrate. This conclusion suggests a strong analogy between the behaviour of O_2^+ and the chemistry of complexed transition metal ions with a d^1 configuration. This analogy is suggestive both concerning the direction of electron movement in collision complexes and in attempts to deduce their geometries. The abundant X-ray structural data on the bonding of small neutral ligands such as N_2,[19] O_2,[20] H_2O,[21] NH_3 [21] and NO [22] to transition metal ions are quite probably directly relevant to the geometries of their gas phase complexes with O_2^+.

The orientation of the O_2^+ ion itself in collision complexes predominantly involving the $3d\pi_g$ orbital can also be suggested from such comparisons. End-on presentation of the O_2^+ ion to a Lewis π acid is probably more favourable than side-on presentation. Not only is the $3d\pi_g$ more polarizable on the long molecular axis,[23] giving a strong

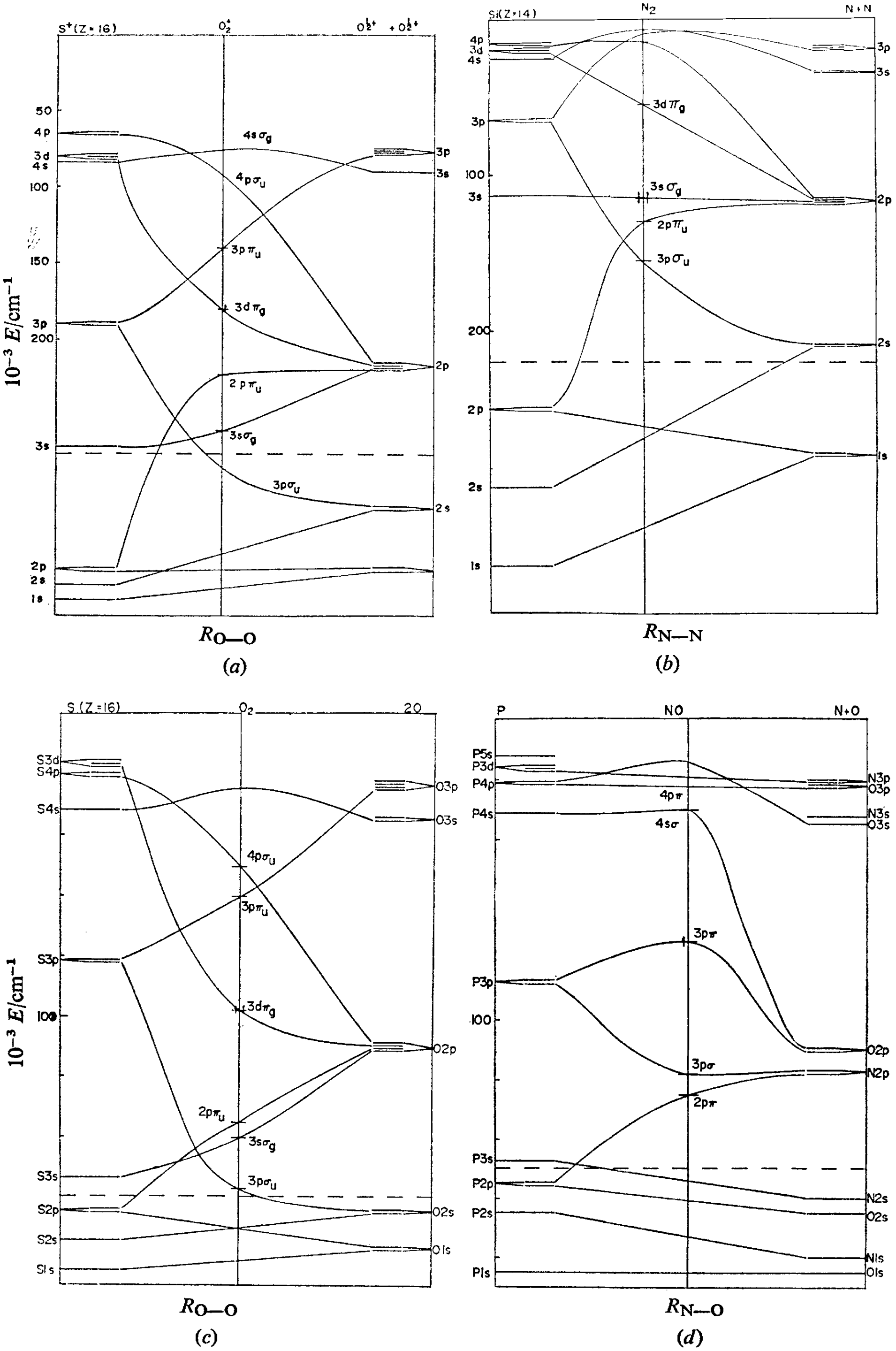


FIG. 1.—United atom correlation diagrams: (*a*) O_2^+; (*b*) N_2; (*c*) O_2; (*d*) NO.

classical preference, but also the ion would achieve greater overlap with the orbitals of the acceptor. End-on geometry presents two $3d\pi_g$ orbitals at approximately 45° to the bond direction while side-on geometry presents one $3d\pi_g$ lobe at 0° and the other at 90° to the bond direction.

The lowest unoccupied orbital, $3p\pi_u$ on the other hand will tend to be an electron acceptor since it correlates strongly downwards from its separated atom limit and has a low APD. In metal complexes, such p orbitals are very seldom involved in π bonding. Rather they act as Lewis σ acid orbitals, accepting charge from a donor molecule, implying side-on presentation of the O_2^+ ion towards Lewis σ bases. This orientation is also favourable classically since interelectron repulsion between the $3d\pi_g$ electron, concentrated at the ends of the molecule, and the charge density of the nucleophilic donor would be minimized.

COLLISION COMPLEX GEOMETRIES AND REACTION CHANNELS

The interaction of O_2^+ with neutral species can be divided into three types. If the classical geometry leads to a favourable orbital overlap, then the ion-molecule reaction will proceed with little or no activation energy. If more than one channel is thermodynamically allowed, preference is usually given to the channel for which the orbital overlap is most favourable. In the absence of thermodynamically allowed (two-body) routes or when such routes are blocked by classical geometry or charge rearrangement barriers, the formation of a complex or cluster ion by three body processes will usually be observed,

$$A^+ + B + M \rightarrow [A \cdot B]^+ + M. \tag{2}$$

Table 1 summarizes the experimentally determined rate constants for a number of ion-molecule reactions of O_2^+ at 300 K in the gas phase. All of the three reaction types mentioned have been observed experimentally.

TABLE 1.—THE CHEMISTRY OF THE O_2^+ ION IN THE GAS PHASE

reation	temperature/ K	rate constant/ cm³ molecule⁻¹ s⁻¹ or cm⁶ molecule⁻² s⁻¹	$-\Delta H^0_{300}$/ kcal mol⁻¹	symmetry allowedness
$O_2^+ + N \rightarrow NO^+ + O$	300	1.8 (−10) [a, b]	96	allowed
$O_2^+ + N_2 \rightarrow NO^+ + NO$	300	<1 (−15) [c]	21	forbidden
$O_2^+ + NO \rightarrow NO^+ + O_2$	300	8 (−10) [b]	65	allowed
$O_2^+ + CH_4 \rightarrow CH_3O_2^+ + H$	300	7.8 (−12) [d]	98	allowed
$O_2^+ + NH_3 \rightarrow NH_3^+ + O_2$	300	2.6 (−9) [e]	44	allowed
$O_2^+ + H_2O + He \rightarrow O_2^+ \cdot H_2O + He$	300	8.5 (−29) [f]		allowed
$O_2^+ + N_2 + He \rightarrow O_2^+ \cdot N_2 + He$	80	1.9 (−29) [f]		allowed
$O_2^+ + O_2 + He \rightarrow O_2^+ \cdot O_2 + He$	200	2.4 (−30) [f]		allowed

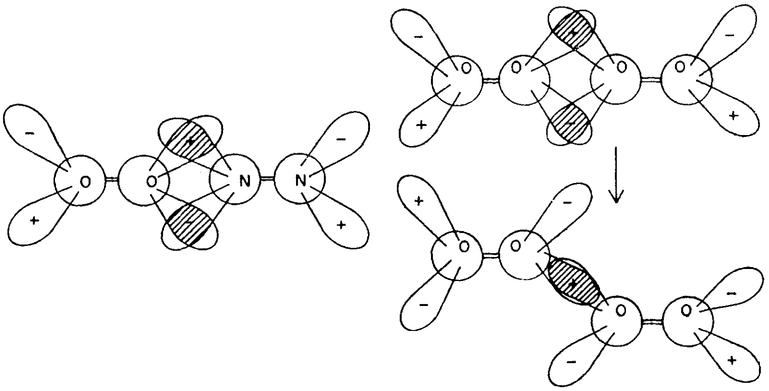
[a] (−10) denotes 10^{-10}; [b] P. D. Goldan, A. L. Schmeltekipf, F. C. Fehsenfeld, H. I. Schiff and E. E. Ferguson, *J. Chem. Phys.*, 1966, **44**, 4095; [c] E. E. Ferguson, F. C. Fehsenfeld, P. D. Goldan and A. L. Schmeltekopf, *J. Geophys. Res.*, 1965, **70**, 4323; [d] D. K. Bohme, R. A. Vane, F. C. Fehsenfeld and E. E. Ferguson, 17th Annual Conf. Mass Spectrometry and Allied Topics, Dallas, Texas (1969), p. 383; [e] D. K. Bohme and F. C. Fehsenfeld, *Canad. J. Chem.*, 1969, **47**, 2715; [f] N. G. Adams, D. K. Bohme, D. B. Dunkin, F. C. Fehsenfeld and E. E. Ferguson, *J. Chem. Phys.*, 1970, **52**, 3133.

(a) π COMPLEXES

(i) N_2.—In collisions of O_2^+ with molecules bearing π frontier orbitals, the classically preferred end-on geometry can be reinforced by covalent overlap if the π orbitals of the neutral molecule are empty. The reaction;

$$O_2^+ + N \rightarrow [O_2 \cdot N_2]^+ \tag{3}$$

in the absence of allowed charged transfer is an example. Using the analogy between O_2^+ and *d* block metal ions, N_2 is expected to bond in an end-on (fig. 2(*a*)) configuration.[19] From infra-red evidence, the metal-nitrogen molecule bond is formed at the expense of the strength of the triple bond of N_2 by acceptance from the metal ion of electron density into the $3d\pi_g$ π acid orbital (fig. 1(*b*)). There is little evidence of donation from the non-bonding $3s\sigma_g$ of N_2 to the metal ion. Square planar or sphenoidal geometry for the $[O_2 \cdot N_2]^+$ complex, derived assuming scalar rather than vector potentials, is much less probable.



(*a*) (*b*)

FIG. 2.—Geometries of π transition states. (*a*) $O_2^+ \cdot N_2$; (*b*) $O_2^+ \cdot O_2$ including relaxation from Jahn-Teller unstable form to a stable geometry.

In the end-on orientation neither O_2^+ nor a *d* block ion can contribute enough antibonding charge to break the N≡N bond.[19] This could only be accomplished with the less favoured side to side collision complex. For this reason the reaction;

$$O_2^+ + N_2 \rightarrow NO + NO^+ \qquad (4)$$

while thermodynamically allowed, is immeasurably slow at thermal energies (table 1).

(ii) O_2.—If the π set of the neutral molecule is partly occupied, covalent interactions at short range may distort the initial classical geometry. Such distortion probably occurs in the collision (fig. 2(*b*)):

$$O_2^+ + O_2 \rightarrow [O_2 \cdot O_2]^+. \qquad (5)$$

Here, the half filled $3d\pi_g$ of O_2 (fig. 1(*c*)) is the π donor orbital but complete charge transfer is impossible and a complex is observed with a bond strength of 0.4 eV.[24] It is probable, since these complexes are so weakly bonded, that the covalent stabilization is insufficient to cause spin pairing (i.e., the system can be treated in the " weak field " model).[25] The complex in end-on geometry would retain an antibonding electron which forces the system to distort (fig. 3) against the classical geometry to minimize the repulsion energy. The equilibrium is probably C_{2h} symmetry and this implied geometry is confirmed by a recent CNDO calculation.[26] The formation of a square D_{4h} complex would be classically much less favourable since the long axis polarizability of O_2 is twice that on the short axis.[23]

(iii) CH_4.—A slightly different aspect of the requirements of symmetry is found in the reaction,

$$O_2^+ + CH_4 \rightarrow [O_2 \cdot CH_3]^+ + H. \qquad (6)$$

Here charge transfer is endothermic but methyl abstraction occurs slowly. Methane possesses no permanent dipole and because of its symmetry does not display a unique axis of polarization. In comparison to collisions of ions with the other first row hybrides, the classical attraction forces acting on methane are therefore much reduced. Because there is no dipolar directing influence, the geometry of the transition complex is essentially random. The rate at which favourable overlap is achieved is statistical and much slower than that of the directed systems involving diatomic molecules.

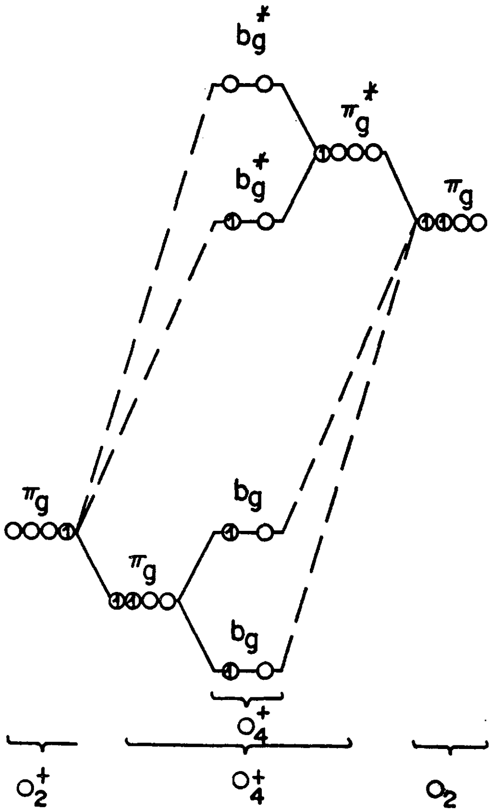


FIG. 3.—Molecular orbital diagram of the linear (Jahn–Teller unstable) and distorted forms of $O_2^+ \cdot O_2$.

The quantal contributions to the rate of reaction are also significantly reduced. From the UA correlation diagram of methane [8] the highest occupied orbital, originating on the hydrogen 1*s* group orbitals, is $2pt_2$. This orbital is observed at 13.0 eV [27] and is therefore antibonding by 0.6 eV with respect to separated hydrogen atoms.[28] The second highest occupied orbital is $2sa_1$, originating on the carbon 2*s* orbital. It is found near 24 eV,[27] which is strongly bonding with respect to the one-electron ionization potential of the carbon 2*s* orbital at 19.3 eV.[28]

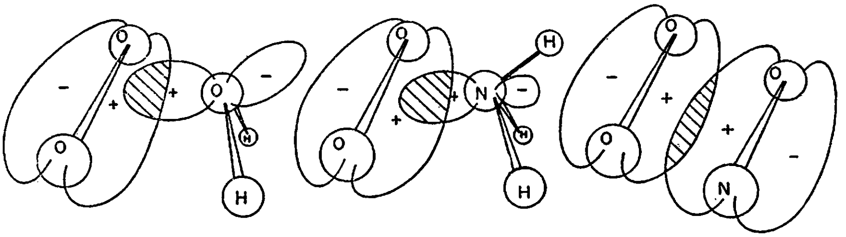
The reaction with O_2^+ is probably initiated by donation of one lobe of $2pt_2$. This creates a distinct three-fold major axis and in C_{3v} symmetry the $2pt_2$ orbital is subduced to 2*pa* and 2*pe* orbitals. The $2pa_1$ can donate into either one lobe of $3p\pi_u$ in a side-on geometry or, less favourably, into $4p\sigma_u$ in an end-on complex. Again the analogy with transition metal complexes may be used. The most stable relevant systems are $Ti(CH_3)_4$ and $W(CH_3)_6$.[29] In both cases the metals have high Lewis π acidity in the empty $d\pi$ orbitals and this strongly suggests that donation of π charge by the $2pe$ orbital of the methyl group is an important part of the bonding. In contrast to the σ component, the best π overlap is achieved in the end-on geometry since both lobes of $3d\pi_g$ are involved. Since the π orbitals on the substrate are filled and approximately 10 eV less stable than the $3d\pi_g$ of O_2^+, (fig. 1 and 2) the latter can act in this case as a π acceptor orbital and promote an end-on geometry of the complex. Thus the most favourable σ and π overlaps are achieved in different geometries but since there is some σ donation possible for the end-on but very little π donation in the side-on orientation the end-on geometry is probably preferred. In either case, the driving force for the reaction is clearly the antibonding nature of the $2pt_2$ orbital and the reaction is very similar to the ready loss of hydrogen from phosphine in mild oxidizing conditions. In this latter case the highest occupied orbital is again associated with the hydrogen group orbitals and is very strongly antibonding in nature.[13]

(*b*) SIGMA COMPLEXES

(i) NH_3.—Collisions of O_2^+ with the σ donor ammonia [13] lead directly to charge transfer (table 1):

$$O_2^+ + NH_3 \rightarrow O_2 + NH_3^+ \tag{7}$$

without evidence of a stable complex. There has been no attempt reported to observe possible emission of radiation during this reaction which would support donation into the $3p\pi_u$ orbital (fig. 4(*b*)). Clearly end-on orientation of O_2^+ yields a cancelling overlap of $3d\pi_g$ with the strongly destabilized $2pa_1$ donor orbital of ammonia. However, if charge transfer occurs at very long range, before the collision geometry is fixed, it could proceed into one lobe of the $3d\pi_g$ yielding a ground configuration O_2 molecule.



(*a*) (*b*) (*c*)

FIG. 4.—Geometries of σ transition states. (*a*) $O_2^+ \cdot H_2O$; (*b*) $O_2^+ \cdot NH_3$; (*c*) $O_2^+ \cdot NO$.

(ii) H_2O.—Charge transfer from water to O_2^+ is endothermic and a stable complex is observed. The predicted collision complex geometry is the side-on orientation of O_2^+ towards the oxygen of water (fig. 4(*a*)). The hydrogen atoms are most probably bent away from the plane of the three oxygen atoms since the antibonding b_2 water donor orbital is at right angles to the plane of the molecule.[13]

(iii) NO.—Collisions of O_2^+ with NO lead to charge transfer. The collision complex is probably a σ type, initially involving donation from one lobe of $3p\pi$ of NO (fig. 1(*d*)) and mutual side-on presentation of the two molecules, (fig. 4(*c*)). At close range, the non-bonding $3p\sigma$ orbital of NO which is centred on the nitrogen can also donate. This covalent interaction would tend to rotate the NO molecule and result in the bent geometry observed in metal complexes.[22] In either case, donation into the $3p\pi_u$ orbital of O_2^+ would again lead to possible emission which could be sought experimentally.

(iv) N.—The collision of atomic nitrogen and O_2^+ is unassisted by a permanent dipole on the substrate. The most probable geometry is the statistically favoured side-on array. In this C_{2v} symmetry the molecular orbitals $b_1(2p_x, 3d\pi_{gx})$; $a_2(3d\pi_{gy})$; $a_1(2p_z, 3p\pi_{zu})$ and $b_2(2p_y, 3p\pi_{uy})$ can form in order of decreasing stability. Since the N atom exists in a quartet ground state the initial configuration of the complex will tend towards $(b_1^1a_2^1a_1^1b_2^1)$. The greatest covalent stabilization can be achieved in the σ type a_1 orbital because its overlap is established at the longest range. This initial configuration, however, is highly excited. At shorter range as the other overlaps become established, the electrons originally on the nitrogen can fall by either emission or radiationless transitions towards a configuration $(b_1^2a_2^2a_1b_2)$. This fills the π antibond of O_2^+, and is consistent with the observed rapid reaction ;

$$O_2^+ + N \rightarrow NO^+ + O. \tag{8}$$

PERTURBATIONS OF FIRST ORDER RULES

The present model has considered both the separated species and the collision complex to be in their ground electronic configurations. This is the conventional assumption for collisions in thermal systems[11] but if the ground state reaction is symmetry forbidden it may still proceed at a very much slower, temperature dependant rate through vibronic coupling. Such temperature dependence may be observed even if overlap is allowed classically and quantally because overlap is negligible.[9] Overlap between such orbitals can be effectively enlarged through vibronic coupling but the vibration must be totally symmetric.

Photolytic reaction routes can be treated in the same way as reactions in ground states. The excited state charge distribution will imply both different classical potentials and orbital donor or acceptor ability. As an example, the excited $(3s\sigma_g^1\ 3p\pi_u^1)$ configuration of molecular nitrogen implies increased polarizability across the bond and side to side geometry of the collision complex. The occupied $2p\pi_u$ orbital of N_2 is less stable than the empty $3p\pi_u$ level of O_2^+ (fig. 1(*a*) and (*b*)). In the side to side complex geometry overlap between these orbitals is established and electron donation can occur into the strongly acidic $3p\pi_u$ of O_2^+. This initial donation weakens the π bond of N_2 but the excited complex can then decay to fill the antibond of O_2^+ in its ground state. The electron movement thus destroys the π bonds in both reagents simultaneously and can initiate the thermodynamically allowed reaction

$$O_2^+ + N_2 \rightarrow NO^+ + NO$$

which is forbidden for the reagents in their ground states.

CONCLUSIONS

In some cases the rates of thermodynamically allowed reactions are unobservably slow for collisions of reagents in their ground states. The kinetic barriers can be analysed in terms of the symmetry conditions applicable to the mutual interaction of frontier orbitals on the reagents but this technique alone may not distinguish between several possible mechanisms. Consideration needs to be given to the presence of classical dipolar interactions in determining the angular relationship of the two bodies during collision. These classical potentials may either reinforce the short range quantal potentials implicit in the symmetry rules, in which case reactions may be rapid, or they may prevent orbital overlap, permitting only unproductive collisions or secondary reactions such as complex formation.

The quantal contributions in small molecules or ions can be described using a one-centre m.o. model. This approach defines the Lewis acidity or basicity of the frontier orbitals quite clearly in terms of changes in stability from the separated atom limit. This allows orbitals, relevant to the mechanism in terms of symmetry, localization and energy, to be quickly identified. It further leads to the concept of an analogy between small diatomic positive ions and transition metal ions which is very useful in assessing and predicting the quantal influences on the geometries of gas phase collisions and complexes.

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