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Complexes of Molecular Oxygen with Organic Molecules

A.L.Buchachenko

Molecular oxygen forms complexes with organic molecules. Evidence for such complex formation and its manifestations are described and criteria are formulated whereby one can distinguish the usual equilibrium complexes from impact (collision) complexes. The principal types of complexes and the electron orbitals with the aid of which the species combined in the complex come into contact are examined.
The bibliography includes 30 references.

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I. INTRODUCTION

Molecular oxygen is a participant in an enormous number of physical and chemical processes. The question whether it reacts as a free molecule or whether its reactions are preceded by some kind of interaction, physical or "semichemical", with the other reactants or with other molecules is important for the chemistry of oxidation processes (where the involvement of oxygen in the initiation of thermal and photochemical oxidation is important), for the photonics of molecules (where oxygen participates in the quenching of electronically excited states, energy transfer, and sensitisation), and for the optical properties and the chemistry of the atmosphere (photochemical reactions of oxygen, the change in the transparency of the atmosphere as a result of the optical absorption by the possible oxygen complexes, etc.)

This review discusses the following question: in what state is molecular oxygen present in organic liquids and does it interact with organic molecules and how does such interaction take place—via the formation of "normal", equilibrium complexes or in contact pairs where the overlap of the electron shells of the reacting species takes place only at the instant of contact between them on collision (this state of the pair is sometimes referred to as an impact or collision complex). The spectroscopic manifestations (in electronic and magnetic resonance spectroscopy), which permit conclusions concerning the nature of the oxygen complexes and about the electron orbitals involved in complex formation, are examined: the chemical manifestations and chemical consequences of the complex formation reactions of oxygen and of its solvation by organic molecules are discussed.

II. ELECTRONIC SPECTROSCOPY AND NMR OF THE OXYGEN COMPLEXES

The manifestations of the formation of complexes between molecular oxygen and organic molecules were first observed by electronic spectroscopy. Evans[1,2] was the first to observe a marked increase of the intensity of the bands corresponding to the forbidden S_0-T_1 transition in the absorption spectra of aromatic hydrocarbons under the influence of dissolved oxygen. It was shown that the vibrational structures of these bands and of the phosphorescence spectra of the hydrocarbons are identical: even the positions of the 0–0 transitions coincide. Both these findings demonstrate reliably that oxygen induces the removal of the spin prohibition of the electronic transitions in many aromatic molecules:[3] it is also clear that the removal of the spin prohibition requires contact between the molecules and the merging of the electron clouds of the molecules of O_2 and the other reactant.

Another manifestation of the complex formation is the appearance of a new structureless absorption band at $\lambda \geq 300$ nm, which is attributed to the complex of O_2 with an aromatic molecule and is believed to be a charge-transfer band. For benzene, $\varepsilon_{max} \cong 900$ at the maximum of this band, while $\varepsilon_{max} \cong 0.4$ for the S_0-T_1 band.[3] Such bands have also been observed for many other compounds—alcohols, ethers, and saturated hydrocarbons. A band at 340 nm has been observed for the O_2 + naphthalene system and has been interpreted as one corresponding to the simultaneous electronic transition of the O_2 molecule to an excited singlet state and of the naphthalene molecule to a triplet state with retention of the overall spin and energy.[3] All these features indicate the occurrence of an interaction of the O_2–organic molecule pair which entails the merging of the electron clouds of the reacting species. The state of the pair in which this interaction takes place is short-lived and the interaction itself is apparently weak.

The nature of the complexes remains obscure. It has been suggested that the species combined in the complex are linked by van der Waals forces, but this conflicts with the spectroscopic characteristics of the complex formation. It is also not confirmed by measurements of the nuclear paramagnetic relaxation of ethylene and ethane in the gas phase in the presence of O_2:[4] the marked difference between the polarisabilities of these molecules is in no way manifested in the nuclear relaxation, which rules out any serious contribution by the van der Waals interaction.

Razuvaev and co-workers used the phenomenon of the quenching of the luminescence of excited molecules by oxygen to investigate the interaction of the latter with organoelemental compounds.[5–8]. It is known that oxygen quenches excited states in both gaseous and liquid phases with a high efficiency and this fact also indicates the occurrence of an interaction between the electron clouds of the oxygen and

excited molecules†. It is most probable that the complexes formed under these conditions are of the donor–acceptor type in which the reacting species are combined via specific orbitals with formation of "semichemical" bonds between them. A partial charge transfer between the species apparently takes place in such a complex but the question whether this state is a collision complex or a normal, equilibrium complex cannot be resolved unambiguously solely from electronic spectroscopic evidence.

Razuvaev and co-workers measured the luminescence intensity of solutions of organoelemental molecules in hexane frozen at 77 K and compared such intensities with solutions containing oxygen and deoxygenated solutions. In the presence of oxygen the intensity of the luminescence of the molecules falls markedly. If it is assumed that the O_2 complexes do exist and that they do not luminesce, it is easy to derive a relation between the luminescence intensity in the presence of oxygen (I) and in its absence (I_0) and the concentration (or pressure) of oxygen:

$$I_0/I = 1 + K[O_2]; \; I_0/I = 1 + K\gamma p_{O_2} \quad , \qquad (1)$$

where γ is the Henry constant for the solubility of oxygen (the authors adopted $\gamma = 1.5 \times 10^{-2}$ mol litre^{-1} atm^{-1} for hexane) and K is the complex formation equilibrium constant for the organic molecule M:

$$M + O_2 \overset{K}{\rightleftarrows} M \cdot O_2 \quad .$$

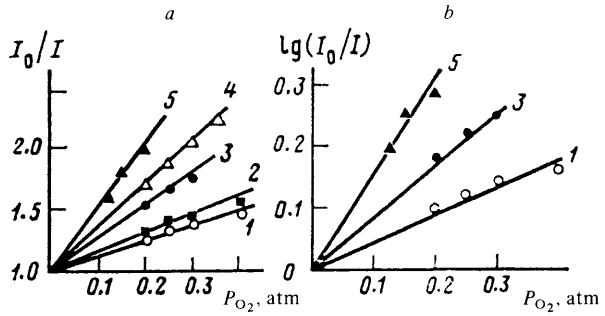
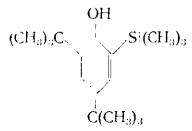
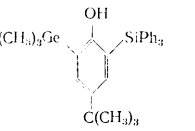
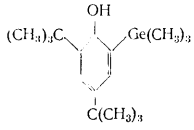
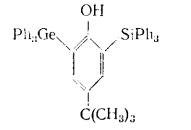
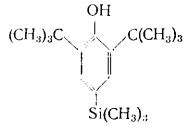
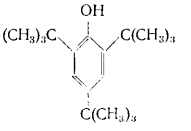
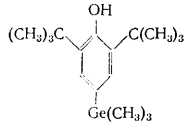


Figure 1. Dependence of the intensity of the fluorescence of organoelemental molecules on the oxygen pressure in terms of the variables of Eqns.(1) (*a*) and (2) (*b*): 1) Ph_4Si; 2) Ph_4Ge; 3) Ph_4Sn; 4) Ph_3SiH; 5) Ph_4Pb.[6]

Eqns.(1) resemble in their form the familiar Stern–Volmer equation and are indeed valid (Fig.1). The equilibrium constants K have been obtained from them. For the compounds Ph_3E (E = P, As, Sb, or Bi), Ph_4E (E = C, Si, Ge, Pb, or Sn), Ph_3SiH, Ph_3GeH, $(CH_3)_4Sn$, etc., the measured constants K are in the range 90–400 litre mol^{-1}; they are higher for Ph_3N (650 litre mol^{-1}) and for the compound $PhGeH_3$, we have K = 2000 litre mol^{-1}.[6] For organomercury compounds of the type Ph_2Hg, $(C_6F_5)_2Hg$, PhHgCl, $PhHgCCl_3$, etc., the constants K are in the range 250–500 litre mol^{-1};[6] the constants for organoelemental phenols are listed in Table 1.

The experimental technique used to measure the complex formation constants on the basis of the quenching of the luminescence is simple and convenient, but one must be sure that the equilibrium $M + O_2 \rightleftharpoons M.O_2$ is attained at 77 K. On freezing, the diffusion of oxygen is greatly retarded (particularly in a solid solution) and at 77 K there is therefore a possibility that the equilibrium corresponding to a higher temperature becomes "frozen". In other words, at 77 K the $M + O_2$ system may not be at equilibrium. Furthermore, the method presupposes a homogeneous distribution of both oxygen and the luminescing molecules in the solid solution, which necessitates certain precautions when this method is employed.

Table 1. The equilibrium constant for the oxygen complexes of phenols (77 K).[6]

Phenol	K, litre mol^{-1}	Phenol	K, litre mol^{-1}
	300		270
	350		280
	280		380
	300	—	—

†In order to avoid the quenching effect of oxygen in liquid solutions, prolonged evacuation of the latter (up to several days) is required. This fact is frequently accounted for by the existence of stable long-lived oxygen complexes. As will be shown below, this view is in all probability erroneous; the long duration of the quenching effect of oxygen is apparently associated with the presence of other quenching agents—comparatively stable intermediate oxidation products, which gradually decompose in the absence of oxygen (on evacuation). These products are sometimes stable and it is then altogether impossible to eliminate fully the quenching effect by evacuation.

Another feature of the luminescence method for the measurement of the equilibrium constant is that one must rule out the possibility of the static quenching of the luminescence of the molecules by oxygen via the Perren mechanism. The static quenching presupposes that there is a sphere with a radius r around the O_2 molecule within which the luminescence of the molecules is quenched, while outside it no quenching takes place. This quenching mechanism is referred to as the inductive-resonance mechanism; it gives rise to the following relation between the luminescence intensity and the

oxygen concentration c:

$$I_0/I = \exp(\alpha c), \quad (2)$$

where $c = \gamma p_{O_2}$ (mol litre^{-1}) and $\alpha = {}^4/_3\pi r^3 N_A$ (litre mol^{-1}) the overall volume of the quenching spheres (here r is expressed in dm and N_A is the Avogadro number). In terms of the variables of Eqn.(2), the dependence of $\lg(I_0/I)$ on c should be represented by a straight line, from the slope of which it is possible to determine the radius of the quenching sphere r. Fig.1*b* illustrates such relations for certain data taken from Fig.1*a*. Evidently Eqn.(2) sometimes holds just as satisfactorily as Eqn.(1) and in order to distinguish them it is necessary to make measurements over a wider range of concentrations of the quenching agent (oxygen). Only then is it possible to establish whether the decrease in the luminescence intensity is caused by complex formation or by the static oxygen quenching.

It has been shown[9] that oxygen in the presence of benzene does not influence the intensity of the luminescence of organoelemental compounds, i.e. O_2 does not behave as a quenching agent under these conditions. This is an important fact, which implies, firstly, that benzene molecules also form complexes with O_2, competing with the molecules of the organoelemental compounds for oxygen, and, secondly, that the oxygen attached to the benzene molecule is incapable of combining with the molecules of the organoelemental compounds and of quenching their luminescence. These results also demonstrate that the luminescence quenching method used[5-9] to analyse the complex formation by molecular oxygen is apparently not complicated by static quenching processes and that the quenching itself is of the exchange-resonance type, determined by the contact between the electron clouds of the reacting species (as in the analogous processes involving quenching by oxygen in gases and liquids).

Thus electronic spectroscopy reveals a number of features indicating a definite interaction of oxygen with organic molecules: the change in the intensity of the electronic transitions, the removal of spin prohibitions, the appearance of new bands in the electronic absorption spectrum, and the quenching of excited states by oxygen. There exist also arguments in support of the view that this interaction cannot be reduced solely to the universal van der Waals interaction and that it has a specific donor–acceptor character. However, electronic spectroscopy cannot yield more definite information about the nature and dynamics of this interaction; more unambiguous results are provided by NMR spectroscopy.

The oxygen molecule has two π-electron systems in two perpendicular planes passing through its D_{∞},h axis. Each of the π-electron systems incorporates three electrons, two of which form an unshared pair, while the third is a single, unpaired electron.[10] The O_2 molecule has a triplet ground state, i.e. the spins of the two single electrons are added together to give an overall spin $S = 1$. The energy of the magnetic dipole interaction of the single electrons is 33000 G and the spin–lattice relaxation time of the electrons is very short, amounting to approximately 50 μs at 1.5 K and $\lesssim 10^{-12}$ s at 300 K.

If the oxygen in the liquid is not in the free state and is partly linked to other molecules, forming complexes with the latter (so far it is immaterial whether these are the usual or collision complexes), then such interaction is inevitably accompanied by the merging of the electron clouds of the reacting species and the partial transfer of the unpaired electrons of the oxygen to the other species—the ligand. The appearance of an unpaired electron in the organic molecule (in both the usual and collision complexes) creates a local magnetic field at the nuclei and induces a line shift in the NMR spectrum of this molecule (it is referred to as the paramagnetic shift). The local magnetic field of the unpaired electron at the ligand nucleus periodically appears and vanishes because the complex is periodically formed and decomposes; each time the orientation of the unpaired electron and hence the direction of the local magnetic field which it generates at the ligand nucleus is random. This leads to the partial averaging of the local magnetic field. Furthermore, such averaging occurs also in the complex itself if the electron relaxation (the reorientation of the electron spin) is rapid. For oxygen complexes, the averaging of the local field of the electron at the ligand nucleus takes place via both mechanisms—via both the formation and decomposition of the complexes and as a result of the short electron relaxation time ($\lesssim 10^{-12}$ s). As a result of the averaging process, the paramagnetic shift of the NMR signal of the ligand in the complex is given by[11]

$$\Delta_0 = \delta_L - \delta_0 = -a\left(\frac{\gamma_e}{\gamma_n}\right)\frac{\gamma_e S(S+1)H_0}{3kT} = -a\alpha, \quad (3)$$

where δ_0 is the position of the NMR peak of the free molecule [in parts per million (p.p.m.)], δ_L is the position of the same peak in the spectrum of the complex, i.e. when the molecule becomes a ligand, γ_e and γ_n are the gyromagnetic ratios for the electron and the nucleus, H_0 is the external magnetic field strength, S the spin of the paramagnetic species (for oxygen, $S = 1$), and a the electron–nucleus (hyperfine) interaction (HFI) constant characterising the local magnetic field of the electron at the ligand nucleus. The parameter α is defined by Eqn.(3), is temperature dependent, and can be readily calculated; in particular $\alpha = 200$ p.p.m. G^{-1} for protons at 26 °C, for the ^{19}F nuclei at the same temperature, we have $\alpha = 211$ p.p.m. G^{-1}, while at 40 °C $\alpha = 202$ p.p.m. G^{-1}.

The paramagnetic peak shifts in the NMR spectra of organic molecules in the presence of oxygen are an unambiguous and reliable manifestation of complex formation by oxygen—a manifestation of the combination of the electron clouds of the oxygen and organic molecules. The magnitude and direction of the paramagnetic shift depend on the sign of the HFI constant involving the ligand nucleus in the complex. The sign of the HFI constant demonstrates the mechanism whereby the unpaired electron is transferred in the complex from oxygen to the ligand and in which orbitals it is located, while the magnitude of the constant determines the density of the unpaired electron transferred from oxygen to the s shell of the ligand atoms. It is linked to the spin density $\rho(0)$ in the s shell of the atom by the familiar Fermi relation:

$$a = ({}^8/_3)\pi\gamma_e\gamma_n\rho(0). \quad (4)$$

The NMR method makes it possible to solve also another important problem—namely that of the complexes (of the usual or collision types) in which the paramagnetic shifts arise. If the usual complexes are formed and the complex formation equilibrium

$$M + O_2 \overset{K}{\rightleftarrows} M \cdot O_2 \quad (I)$$

is established, as a result of which the organic molecule M is periodically either in a free state, or in the complex $M.O_2$ then the paramagnetic shift Δ of the NMR peak observed experimentally is defined by the equation[11]

$$\Delta = \delta - \delta_0 = \Delta_0 p_L, \quad (5)$$

where p_L is the mole fraction of the complex $M.O_2$. Here δ_0 is, as before, the position of the NMR peak in the spectrum of the free molecule and δ is its position in the presence of

oxygen:

$$\delta = \delta_0 p_0 + \delta_L p_L \ . \qquad (6)$$

Condition (6) describes the averaging of the position of the NMR peak due to the rapid exchange of the molecule between the two states (the free molecule and the ligand in the complex with oxygen), whose mole fractions are p_0 and p_L respectively. Eqn.(5) is obtained taking into account Eqn.(6) and the self-evident normalisation condition $p_0 + p_L = 1$.

After determining p_L on the basis of equilibrium (I), i.e.

$$p_L = \frac{K[O_2]_0}{1 + K[M]_0} \qquad (7)$$

and substituting it in Eqn.(5), we obtain

$$\Delta = \frac{\Delta_0 K[O_2]_0}{1 + K[M]_0} \ , \qquad (8)$$

where $[O_2]_0$ and $[M]_0$ are the concentrations in solution of oxygen and of the other molecules involved in the complex formation. The magnitude of this shift, referred to the concentration $[O_2]_0 = 1$ M (the reduced paramagnetic shift), will be designated by Δ^*:

$$\Delta^* = \frac{\Delta_0 K}{1 + K[M]_0} \ . \qquad (9)$$

Eqns.(8) and (9) can be expressed in a linear form:

$$\frac{[O_2]}{\Delta} = \frac{1}{\Delta_0}(K^{-1} + [M]) \ , \qquad (10)$$

$$\frac{1}{\Delta^*} = \frac{1}{\Delta}(K^{-1} + [M]) \ , \qquad (11)$$

where the subscripts to $[O_2]_0$ and $[M]_0$ have been omitted.

If the paramagnetic shifts arise in collision complexes which exist only when the two species are in contact during the period of their "settled" life, then the mole fraction p_L of such complexes can be easily calculated, provided that one knows the coordination number of the complex n (i.e. the number of nearest neighbours) and the probability that the test molecule M enters the first (contact) coordination sphere of the oxygen molecule:

$$p_L = \frac{[M \cdot O_2]}{[M]} = \frac{n[O_2][M]}{[M] + [N]} \cdot \frac{1}{[M]} = \frac{n[O_2]}{[M] + [N]} \ , \qquad (12)$$

where [N] is the concentration of other molecules in the mixture.

Evidently the concentration dependences of p_L and of the paramagnetic shifts for complexes of these two types differ appreciably. In order to distinguish such complexes, it is sufficient to investigate the concentration dependence of the paramagnetic shift and to test whether Eqns.(10) and (11) or (12) hold.

Finally the third advantage of NMR in the study of the oxygen complexes is the possibility of the direct measurement of the concentration of dissolved oxygen. For this purpose, the paramagnetic shifts are measured in solutions at different concentrations placed in two sealed tubes arranged coaxially one inside the other, the inner tube containing oxygen (under a pressure of 0.1–5 MPa depending on the oxygen concentration which it is desired to ensure in the solution). The concentration of the dissolved oxygen in the inner tube is determined from the distance between the NMR peaks in the spectrum of an inert solvent present in the inner and outer bulbs. The shift δ_χ of the peaks due to the inner tube relative to those of the outer tube is due to the magnetic volume susceptibility of the dissolved oxygen and is related to its concentration $[O_2]$ by the expression[12]

$$\delta\chi = (2\pi/3) \cdot 10^{-3} \chi_m [O_2] \qquad (13)$$

where χ_m is the molar magnetic susceptibility of oxygen:

$$\chi_m = \frac{4N_A\beta^2 S(S+1)}{3kT} = \frac{0.496 S(S+1)}{T} \ . \qquad (14)$$

Here N_A is the Avogadro number, β the Bohr magneton, and S the electron spin of the oxygen molecule; in particular at 26 °C we have

$$\delta_\chi \text{ (p.p.m.)} = 6.94\,[O_2], \qquad (15)$$

where the O_2 concentration is expressed on a molar scale.

Having measured the concentration dependence of the paramagnetic shifts (i.e. their dependence on the mixture composition) and the oxygen concentration, it is possible to test the validity of Eqns.(10)–(12) and to determine the type of complexes formed by oxygen and their quantitative characteristics (the equilibrium constants K and the HFI constants a).

III. OXYGEN COMPLEXES OF ORGANIC AND ORGANOELEMENTAL MOLECULES

The paramagnetic shifts of the NMR peaks induced by molecular oxygen have been observed in many investigations[11, 13–15] for a large number of various organic molecules. They were first observed by Polak and Navon,[13] but, owing to their low magnitude (the authors worked at low pressures up to 0.3–0.4 MPa), it was impossible to reach definite conclusions about the origin of these shifts. The concentration dependences of the paramagnetic shifts at high oxygen pressures were investigated only quite recently and reliable evidence has been obtained for the existence of the oxygen complexes.[11]

Buchachenko and Pokrovskaya[11] were interested primarily in the interaction of aromatic molecules, particularly benzene, with molecular oxygen. Their initial idea was that the interaction of oxygen with benzene would induce paramagnetic shifts of the benzene NMR peaks, which could be reckoned relative to the position of the NMR peaks of cyclohexane—the solvent which is traditionally regarded as inert and which the authors assumed would not interact with oxygen, i.e. its NMR peak would not undergo paramagnetic shifts.

An example of the recording of the NMR spectrum of a benzene–cyclohexane mixture (for the volume ratio $C_6H_6 : C_6H_{12} = 14 : 1$) is illustrated in Fig.2. The narrow peaks are due to benzene and cyclohexane in the bulb without oxygen and the broadened peaks are due to benzene and cyclohexane in the bulb containing oxygen. The oxygen-induced shift of the benzene peak is 172.9 Hz and the shift of the cyclohexane peak is 160.9 Hz. The difference between the shifts is 12.0 Hz and exceeds by two orders of magnitude the error of the measurement. Consequently, apart from the shifts caused by the magnetic susceptibility of the dissolved oxygen (which should be the same for benzene and cyclohexane), there exists also the paramagnetic shift $\Delta = 12.0$ Hz, which, as suggested in the beginning, is caused by the interaction of benzene with oxygen.

However, it is impossible to claim *a priori* which mixture component (benzene or cyclohexane) is inert in relation to oxygen. The paramagnetic shifts of the NMR peaks were therefore determined in the spectra of mixtures of benzene and cyclohexane of different composition and were analysed by two methods: it was initially assumed that cyclohexane is inert and the paramagnetic shifts of the benzene peaks

were reckoned relative to the cyclohexane peak (for example, the shift of 12.0 Hz for the $C_6H_6 : C_6H_{12} = 14 : 1$ mixture is due to benzene in this version). In the second method it was assumed that the paramagnetic shift is undergone by the cyclohexane peak and benzene is the inert solvent and that the ^1H NMR peaks of benzene do not undergo a paramagnetic shift; in this method the shift $\Delta = 12.0$ Hz for the above mixture was attributed to cyclohexane. The paramagnetic shifts Δ were converted into the reduced shifts Δ^*; the oxygen concentrations necessary for this recalculation were determined from total shifts of the NMR peaks of benzene.

The reduced shifts Δ^* are plotted in Fig.3 as a function of mixture composition; its analysis permits the conclusion which component (benzene or cyclohexane) is the one with which oxygen interacts. If it is assumed that the cyclohexane is inert in relation to oxygen, then the shifts of the benzene peaks reckoned relative to the cyclohexane peaks (curve 2) increase with increasing benzene concentration. This relation has no physical significance, since at a constant oxygen concentration the mole fraction of the benzene–oxygen complexes should diminish with increasing benzene concentration because the complexes are diluted by the free benzene molecules. As a result, the paramagnetic shift of the benzene peaks should diminish with the increasing benzene concentration; this prediction is completely in conflict with experiment.[11]

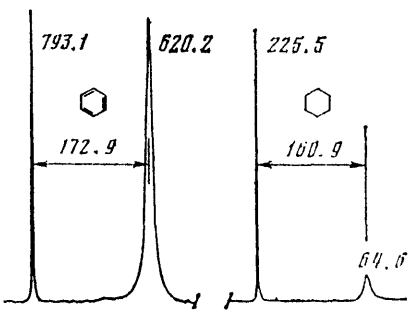


Figure 2. NMR spectrum of the benzene–cyclohexene mixture measured at a frequency of 100 MHz. The numerals opposite the NMR peaks indicate their frequencies (in herz) relative to hexamethyldisiloxane.[11]

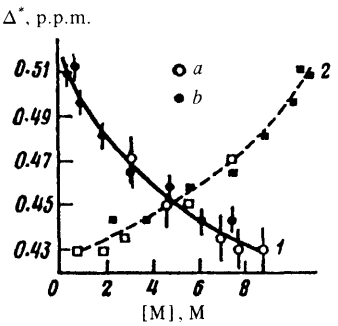


Figure 3. Concentration dependence of the reduced paramagnetic shifts Δ^*: 1) the shifts of cyclohexane peaks relative to benzene lines; 2) the shifts of benzene peaks relative to cyclohexane lines; temperature (°C): *a*) 20; *b*) 10.[11]

On the other hand, if it is assumed that the benzene molecules are inert with respect to oxygen, then the concentration dependence of the shifts of the cyclohexane peaks reckoned relative to the positions of the benzene peaks has the correct form: the mole fraction of the cyclohexane complexes and hence the shifts of the cyclohexane peaks diminish with increasing cyclohexane concentration. (Fig.3, curve 1). Furthermore, the concentration dependence of the paramagnetic shifts of the cyclohexane peaks obeys Eqn.(11) (Fig.4); the equilibrium constant for the complex formation reaction between cyclohexane and oxygen, calculated by Eqn.(11), is 1.6×10^{-2} litre mol^{-1}, while the HFI constant for the complex, averaged over all the ligand (cyclohexane molecules) protons is positive (the peaks shift in a weak field) and amounts to +0.15 G. If it is assumed that the transfer of the unpaired electron from oxygen in the complex takes place to only one of the twelve ligand hydrogen atoms (the bond between oxygen and the ligand is formed via this atom), then the HFI constant for this atom amounts to $0.15 \times 12 = 1.8$ G, which corresponds to the unpaired electron density in the 1s orbital of the hydrogen atom (approximately 0.36×10^{-2}). We may note that this density is positive, i.e. the unpaired electrons are transferred from oxygen to the ligand hydrogen atom via a delocalisation mechanism.

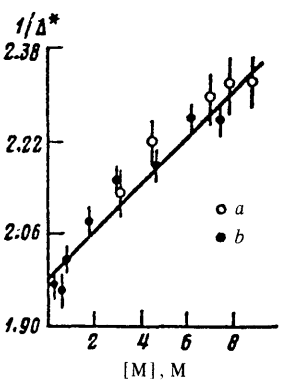


Figure 4. Dependence of the reciprocal of the reduced paramagnetic shift of the NMR peak of cyclohexane on its concentration in terms of the variables of Eqn.(11); temperature (°C): *a*) 20; *b*) 10.[16]

Thus it follows unambiguously and reliably from the analysis of the concentration dependence of the paramagnetic shifts that the cyclohexane NMR peaks shift to a greater extent under the influence of oxygen than do the benzene peaks. Since the paramagnetic shifts of the cyclohexane peaks are small, those for benzene are smaller still and in principle can be neglected and one can assume that the benzene peak does not undergo a paramagnetic shift at all. In terms of this approximation, benzene can be regarded as an inert solvent in the sense that its peak in the ^1H NMR spectrum hardly shifts and can be used as the reference signal for the measurement of the paramagnetic shifts of the peaks of all other molecules. Furthermore, it follows from this that the shift of the benzene peak is caused almost wholly by the magnetic volume susceptibility of the dissolved oxygen (Buchachenko and Pokrovskaya[11] gave direct experimental evidence for this fact) and can be used to measure its concentration.

Another important result consists in the fact that the interaction of oxygen with cyclohexane (and, as will be shown below, also with other molecules) takes place in the usual complexes and not in collision complexes, which is indicated by the validity of Eqns.(10) and (11) for the concentration dependence of the paramagnetic shifts. The same dependences hold for the paramagnetic shifts of the NMR peaks of the protons of *p*-difluorobenzene in benzene. The complex formation equilibrium constant is 0.25 litre mol^{-1} and the HFI constant for the protons is −0.01 G.

The absence (or more precisely the negligible magnitude) of the paramagnetic shifts of the proton NMR peaks for benzene does not strictly speaking imply that benzene is inert in relation to oxygen and is not involved in complex formation reactions with the latter. The absence of a shift can be a consequence of the fact that benzene forms with oxygen complexes of different types (for example via the C−H bond and the π-electron system) and the paramagnetic shifts of the proton signals induced in these complexes have different signs so that on average they fairly effectively cancel out. In order to test this hypothesis, the paramagnetic shift of the ^{13}C NMR peak of benzene was measured. In the benzene spectrum at 24 °C the shift $\Delta(^{13}C)$ was 0.49 p.p.m. at an O_2 concentration (determined from the shift of the proton resonance peak) of 0.123 M. Hence it follows that the reduced paramagnetic shift $\Delta(^{13}C) \cong 4$ p.p.m., i.e. its value is large, exceeding by an order of magnitude the paramagnetic shifts of the signals of the protons in cyclohexane. The presence of such a shift is direct evidence for the formation of a complex between benzene and oxygen. The shift is directed downfield, which implies that in the complex the positive spin density of the unpaired electron is transferred from oxygen to the π-electron system of the benzene molecule and the mechanism of this transfer involves direct delocalisation.

The most complete and reliable results have been obtained by Karmilov and co-workers,[14,15] but the paramagnetic shifts were measured in these investigations relative to the position of the NMR peak of cyclohexane, which was assumed to be inert with respect to oxygen. Bearing in mind the results of Buchachenko and Pokrovskaya[11] and introducing corrections for the paramagnetic shift of the cyclohexane peaks, it is now possible to find the true paramagnetic shifts for these molecules relative to benzene; the negative shifts correspond to an upfield displacement of the NMR lines, while the positive shifts correspond to a downfield displacement (Table 2). The difference between the signs and magnitudes of the paramagnetic shifts is striking. This fact constitutes the strongest evidence that the paramagnetic shifts are induced in the usual complexes of the molecules with oxygen and not in collision complexes, where the paramagnetic shifts are induced by the van der Waals interaction and should have the same sign for all the nuclei regardless of the chemical species to which they belong.

It is seen from the data in Table 2 that the signs and magnitudes of the paramagnetic shifts depend on the chemical structure of the ligand and obey definite rules. The NMR peaks of the protons in the OH and NH groups (in water, alcohols, and aniline, and pyrrolidine) as well as the CH groups in chloroform and CH_2Cl_2 undergo an upfield paramagnetic shift, i.e. in the complexes with oxygen the negative spin density of the unpaired electron appears on these protons. The signals of the protons of the aliphatic CH_2 and CH_3 groups (in alcohols, cyclohexane, hexamethylbenzene, dimethylaniline, *o*- and *p*-xylenes, tetramethyl-*p*-phenylenediamine, and cyclohexene) undergo downfield paramagnetic shifts, i.e. the positive spin density of the unpaired electron is transferred to these protons in the complex with oxygen.

Finally, the signals of the protons of aromatic rings (in toluene, *o*- and *p*-xylenes, *p*-difluorobenzene, naphthalene, and tetramethyl-*p*-phenylenediamine) undergo upfield paramagnetic shifts, which indicates the appearance of a negative spin density on these protons in the oxygen complex.

Table 2. The paramagnetic shifts Δ* of the NMR peaks of the molecules induced by the formation of their complexes with oxygen.

Molecule (ligand)	Group	Δ*, p.p.m.	Molecule (ligand)	Group	Δ*, p.p.m.
Water (in acetone)	OH	−0.52	*o*-Xylene	CH_3	+0.33
Methanol	OH	−0.32		⩾CH	−0.03
"	CH_3	+0.33	*p*-Xylene	CH_3	+0.34
Ethanol	OH	−0.52		⩾CH	−0.18
"	CH_2	+0.49	*p*-Difluorobenzene	⩾CH	−0.14
"	CH_3	+0.33	$(CH_3)_2N-C_6H_4-N(CH_3)_2$	CH_3	+0.35
Chloroform	CH	−0.42	"	⩾CH	−0.20
CH_2Cl_2	CH_2	−0.32	Cyclohexene	α-CH_2	+0.55
Phenylacetylene	≡CH	−0.52	"	β-CH_2	+0.40
$PhNH_2$	NH_2	−0.62	"	⩾CH	+0.10
Pyrrolidine	NH	−0.17	Cyclo-octadiene	CH_2	+0.37
Acetone	CH_3	+0.05		⩾CH	+0.20
$(CH_3)_3SiOSi(CH_3)_3$	CH_3	+0.02	Cyclo-octatetraene	⩾CH	+0.07
Cyclohexane	CH_3	+0.42	Naphthalene	α-CH	−0.43
Hexamethylbenzene	CH_3	+0.18	"	β-CH	−0.10
$PhN(CH_3)_2$	CH_3	+0.23			

These findings permit definite conclusions about the structure of the oxygen complexes and the nature of the orbitals involved in the "joining together" of the species in the complex. Molecules containing the OH and NH groups as well as those of $CHCl_3$ and CH_2Cl_2 add to the unshared electron pair of oxygen via their O−H, N−H, or C−H bonds (Fig.5*a*). These are complexes of the *n*−σ type (or hydrogen bonded complexes), in which oxygen provides the *n* orbital and the ligand the σ orbitals of the O−H, N−H, or C−H bonds. The negative spin density on the hydrogen atom of the bond involved in complex formation (O−H, N−H, or C−H) appears in this complex as a result of the spin polarisation of the hydrogen bond by the unpaired π electron of the oxygen molecule. The structure and the electronic interactions of these oxygen complexes resemble those of the anlogous complexes with participation of organic radicals.[16,17]

The aliphatic CH_2 and CH_3 groups add via the C−H σ-bonds to the π orbital of oxygen, forming π−σ complexes (Fig.5*b*); as a result of delocalisation, a positive spin density appears on the hydrogen atom of the ligand (as in the radical complexes of the same type[17]) and there is a downfield paramagnetic shift (in cyclohexane, the methyl groups of alcohols, amines, xylenes, toluene, etc.).[16]

Aromatic molecules apparently add via the π-electron system to the π orbital of oxygen, forming a π−π complex (Fig.5*c*); the unpaired π electron is then partly transferred to the π-electron system of the ligand from oxygen and induces, via the spin polarisation of the C−H bonds, a negative spin density in the 1*s* orbitals of the hydrogen atoms of the aromatic ring. The negative paramagnetic shifts for the aromatic protons in substituted benzenes and in naphthalene can be explained in precisely this way. This is also supported by the positive paramagnetic shift (downfield) of the signals of the ^{13}C nuclei of benzene (see above), indicating the appearance of a positive π-electron spin in the π-electron system of benzene.

However, we may note that the paramagnetic shifts of the peaks due to aromatic protons are small in absolute magnitude and those for benzene are altogether negligible, which implies that benzene (and apparently other aromatic molecules) form

complexes of two types: $\pi-\pi$, in which a negative spin density appears on the protons, and $\pi-\sigma$ (as for cyclohexane), in which a positive spin density appears on the protons via direct delocalisation. The almost complete and mutual cancellation of these two contributions for benzene ensures that the overall paramagnetic shift of the benzene protons is zero. In other paramagnetic molecules this cancellation is incomplete with the contribution by the $\pi-\pi$ complex predominating and an upfield paramagnetic shift.

The mutual cancellation of the paramagnetic shifts due to various complexes apparently takes place also for the acetone and hexamethyldisiloxane protons, for which the paramagnetic shifts are very small. In this case the positive shift due to the $\pi-\sigma$ complexes is compensated by the negative shift due to other complexes (for example, $n-\sigma$).

Special mention should be made of the paramagnetic shift of the signals due to the protons of double bonds (cyclohexene, cyclohexadiene, and cyclo-octatetraene). These shifts are directed downfield, are small in absolute magnitude, and depend on the chemical structure of the ligand. In these instances, too, two contributions are added together: the positive contribution due to the $\pi-\sigma$ complexes (via the direct delocalisation of the spin from the π orbital of oxygen to the C–H σ-bond (Fig.5*b*) and the negative contribution due to the $\pi-\pi$ complexes (delocalisation of the π-electron density from oxygen to the π-electron system of the double bond with subsequent spin polarisation of the C–H bonds attached to the double bond). The same mutual cancellation takes place in this instance as for aromatic protons; the only difference is that the $\pi-\sigma$ interaction makes the dominant contribution. The involvement of the double bonds in $\pi-\pi$ interaction and the presence of the positive spin density of the unpaired π-electron in the π-electron system of the double bonds are indicated by the considerable positive shift of the protons in the α-CH_2 group in cyclohexene, which exceeds that due to the protons of the β-CH_2 group. This additional positive shift of the signal of the α-CH_2 protons arises owing to the direct delocalisation of the unpaired π electron from the double bond to the α-CH_2 group via the hyperconjugation mechanism.

The π-electron spin density is also transferred from oxygen to the π-electron system of phenylacetylene (Table 2) as a result of $\pi-\pi$ interaction. It then induces, via spin polarisation, a negative spin density on the acetylene proton, which is accompanied by an upfield paramagnetic shift of the peak due to the latter.

The concentration dependence of the paramagnetic shifts has been investigated in mixtures of benzene with cyclohexane, *p*-xylene, cyclo-octadiene, hexamethyldisiloxane, *p*-difluorobenzene, and acetone. In most cases the dependence proved to be very weak and difficult to measure; this implies that the complexes with oxygen are weak and their stability constants at 20 °C are small and satisfied the condition $K[M] \ll 1$, i.e. $K \lesssim 10^{-2}$ litre mol^{-1}; for these complexes, $\Delta^* = \Delta_0 K$ (Table 2). The concentration dependence of the paramagnetic shift could be measured and the equilibrium constant and the constant for the hyperfine interaction in the complex could be determined only for cyclohexane and *p*-difluorobenzene.[11,16]

The paramagnetic shifts of the nuclei belonging to different fragments of the same molecule are different (Table 2). Thus in toluene the shifts for the aromatic and methyl protons are different not only in magnitude but also in sign. The same is characteristic of methanol, ethanol, xylene, and naphthalene, which implies that different structural elements of the same molecule interact with oxygen in different ways. Furthermore, the temperature dependences of the shifts for different groups of the same molecule are likewise different. Thus the shifts for the methanol methyl protons depend only slightly on temperature, while for the hydroxyl proton the temperature coefficient of the shift is 0.5 kcal mol^{-1}; in toluene the shifts for aromatic protons are almost independent of temperature, while for the methyl protons their dependence is pronounced with a temperature coefficient of 1.7 kcal mol^{-1}.[15]

The different temperature dependences of the shifts for different functional groups in the same molecule imply that the molecules interact with oxygen via individual fragments and not as a single whole, i.e. the interaction has a specific localised character. Furthermore, both these facts, namely

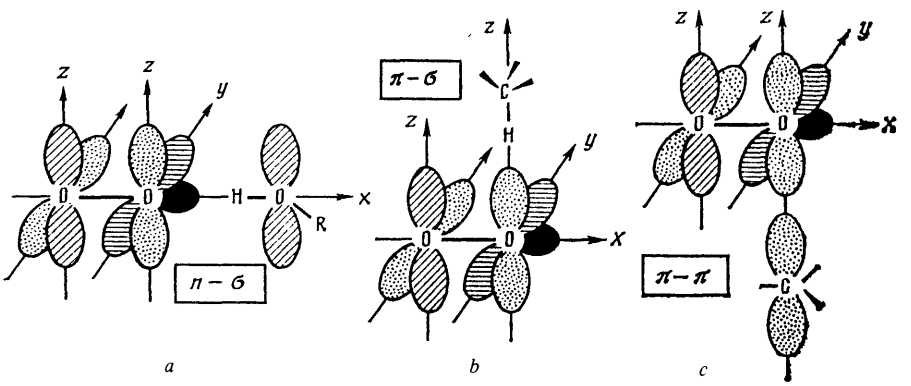


Figure 5. Molecular models of the oxygen complexes: *a*) the $n-\sigma$ complex in which oxygen provides the *n* orbital and the ligand the σ orbital of the O–H, N–H, or C–H bond; *b*) the $\pi-\sigma$ complex in which oxygen provides the π orbital and the ligand the σ orbital of the bond; c) the $\pi-\pi$ complex in which both oxygen and the ligand provide the π orbitals for the complex formation reaction.[16]

the different shifts and their different temperature dependences, demonstrate convincingly that the dominant type of interaction in the oxygen–organic molecule pair is equilibrium complex formation. As already stated previously, the paramagnetic shifts induced in collision complexes should be the same both in magnitude and in sign for all nuclei and in addition should be independent of temperature.

An important criterion used in the "recognition" of the complexes and the identification of the orbitals involved in complex formation is the competition between two or more ligands for the oxygen orbitals. This criterion was formulated in the analysis of the structures of radical complexes.[18] The idea is that the concentration dependences of the paramagnetic shifts of the solvated molecules depend on whether two different ligands add to the same oxygen orbital or to different orbitals. In the former case the ligands compete for their "site" in the given oxygen orbital, while in the latter they do not compete and add independently and autonomously to different orbitals. Clearly in the case of non-competing ligands the addition of one ligand should not influence the paramagnetic shifts of the signal due to the other ligand. On the other hand, such an influence should occur for the competing ligands, tending to "sit" on the same electronic orbital of oxygen. Thus it follows from the concentration dependence of the cyclohexane shifts in the presence of acetone, water, and tetramethylsilane that cyclohexane is a stronger ligand than water.[14] The molecules of methanol (hydroxy-group) and CCl_4 are not competing ligands, i.e. they add to different oxygen orbitals: the OH group of methanol adds to the *n* orbital and CCl_4 adds to the π orbital. Dimethylaniline (the CH_3 group) and CCl_4 are competing ligands, both molecules adding via their C–H and C–Cl bonds to the oxygen π orbital.[14]

The experimental results for the paramagnetic shifts of competing ligands are as yet insufficient to reach final conclusions about the detailed structure of the oxygen complexes. However, one can already reach the general preliminary conclusion that the oxygen π orbital is more active in complex formation than the *n* orbital. This property differentiates the oxygen complexes from those of organic radicals: in the latter case the *n* orbitals give rise to more stable complexes with organic molecules than the π orbitals.[17] This feature is apparently associated with the electronic structure of the oxygen molecule, in which the *n* orbitals in the π-electron system have not been formed distinctly and are strongly coupled with the π orbitals of single electrons, while the *n* orbitals of the 2*s* electrons are too "weak" for complex formation.

We may note that, for a number of molecules (acetone, chloroform, and phenylacetylene), considerable paramagnetic shifts of the NMR peaks due to the ^{13}C nuclei have also been observed;[14] this indicates a fairly pronounced overlap of the electron clouds of the interacting species in the oxygen complex and a far-reaching delocalis at ion of the spin density from the oxygen to the ligand. Thus for acetone (^{13}C in the CO group) the paramagnetic shift Δ^* at acetone concentrations of 1.5–4.5 M in benzene amounted to 0.2–0.5 p.p.m.[16] The ^{13}C peaks shifted downfield, indicating that a partly unpaired π electron is transferred to the π-electron system of acetone from oxygen. This transfer apparently proceeds via the π–π interaction (as in the complex with benzene).

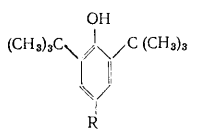
The paramagnetic shifts of the NMR peaks of the protons in diphenyl- and dibenzyl-mercury in the presence of oxygen have been measured[19] relative to cyclohexane. After introducing a correction for the cyclohexane shift, we obtain the true paramagnetic shifts for these organomercury molecules (Table 3).

Since both toluene and xylene form complexes with oxygen, it is evident that the phenyl and benzyl groups in the organomercury molecules should also add to oxygen. However, the marked difference between the paramagnetic shifts of these two groups of molecules (Table 3) shows that the complex formation with the mercury atom is the dominant process and makes the maximum contribution to the paramagnetic shifts for the organomercury molecules. The temperature dependence of the shift has also been measured for dibenzylmercury; the temperature coefficient is approximately 1 kcal mol^{-1}.[19]

Table 3. The paramagnetic shifts Δ^* (in p.p.m.) for the protons (CCl_4, 25 °C).[19]

Molecule	⩾CH	CH_3 (or CH_2)	Molecule	⩾CH	CH_3 (or CH_2)
Ph_2Hg	−0.47	—	Toluene	−0.07	+0.38
$(PhCH_2)_2Hg$	−0.22	−0.12	*o*-Xylene	−0.03	+0.33

The paramagnetic shifts for the protons of a number of phenols (including organoelemental phenols) of the type



have been measured;[20,21] their values, corrected for the paramagnetic shift of cyclohexane, are listed in Table 4.

Table 4. The paramagnetic shifts Δ^* (in p.p.m.) for the protons of phenols (CCl_4, 25 °C).

R	OH	Ring *meta*-protons	R	OH	Ring *meta*-protons
$C(CH_3)_3$	−0.20	+0.13	$Si(CH_3)_3$	−0.38	+0.05
CH_3	−0.12	+0.20	$Ge(CH_3)_3$	−0.64	+0.07
H	−0.14	+0.26	$SiPh_3$	−0.67	—
Cl	−0.25	+0.10	$GePh_3$	−0.97	—
NO_2	−0.57	−0.32			

A common property of the oxygen complexes of these phenols is an upfield paramagnetic shift of the peaks of the hydroxyl protons; this implies that the negative spin density of the unpaired electron appears on the hydroxyl proton in the complex. Evidently oxygen adds to the hydroxy-group of phenol via the unshared electron pair (hydrogen-bonded complex). Furthermore, the positive π-electron density is transferred to the π-electron system of the benzene ring in the complex and is distributed in the π-electron system of the ring in the same way as in aromatic alternant radicals: it is positive in the *o*- and *p*-positions and negative in the *m*-position. A positive spin density should then appear on the *m*-protons as a result of spin polarisation and their NMR signal should undergo a downfield paramagnetic shift (in agreement with experiment, see Table 4).

Another piece of evidence for the appearance of the unpaired π electron in the benzene ring of the ligand is the downfield paramagnetic shift of the signal due to the methyl group in the *p*-position in the spectrum of a phenol with

R = CH_3 (Δ^* = +0.61 p.p.m.); it arises as a result of the delocalisation of the π electron from the *p*-position of the benzene ring via the hyperconjugation mechanism.[20]

It is not clear whether the unpaired electron is transferred from oxygen to the hydroxy-group and to the π-electron system of the benzene ring in the same complex or different complexes (i.e. to the hydroxy-group in complexes of one type and to the π-electron system in those of another). It is incontrovertible that the paramagnetic shifts of the peaks in the spectra of element-containing phenols exhibit anomalies (Table 4), which implies that, apart from the interaction of oxygen with the hydroxy-group and the benzene ring, there is also a direct and significant (in magnitude) interaction of oxygen with the atoms of the elements. This conclusion is likewise valid for other organoelemental phenols investigated by Razuvaev et al.[21]

IV. OXYGEN COMPLEXES OF ORGANOFLUORINE MOLECULES

It is known that organofluorine hydrocarbons and their derivatives dissolve molecular oxygen effectively and are therefore used to transport the latter in blood substitutes and in liquid-phase respiration.[22,23] The state of oxygen in these solutions and the causes of its anomalously high solubility are unknown. The hypothesis has been put forward that organofluorine liquids have a "porous" structure with a large free volume which is accessible to oxygen, but it lacks any kind of foundation.

It is most likely that oxygen in organofluorine liquids exists in a state where it is partly bound in complexes. In order to test this hypothesis, a study was made of the paramagnetic shifts of the ^{19}F NMR peaks in the spectra of organofluorine molecules in the presence of dissolved oxygen.[24] Very large paramagnetic shifts were observed and their concentration dependence was found to obey Eqn.(11) (Fig.6), whence the complex formation equilibrium constants and the HFI constants for the ^{19}F nuclei were obtained (Table 5). Compared with the paramagnetic shifts of the ^{19}F NMR peaks, the proton resonance shifts of the molecules of compounds 2, 3, and 4 (Table 5) are negligible, i.e. the CH_2 and CH_3 groups and the double bonds are hardly involved in complex formation with oxygen, which implies that the interaction of oxygen with the molecules is localised exclusively at the fluorine atoms. The positive spin density is then transferred to the electronic orbitals of the fluorine atom (there is a downfield shift of the ^{19}F lines and the constant *a* is positive). The positive sign of the constant *a* implies that an interaction of the π–*n* type takes place in the complex, i.e. the π orbital of oxygen adds to the unshared electron pair of the fluorine atom. Approximately 0.1% of the unpaired electron is then transferred to the inner 2*s* shell of the fluorine atom.

Table 5. The equilibrium constants *K* and the HFI constants *a* for the complexes of O_2 with organofluorine molecules (40 °C).

No.	Molecule	*K*, litre mol^{-1}	*a*, G
1	C_6F_6	0.13±0.01	+0.49
2	$(CF_3)_3CCH{=}CH_2$	0.12±0.01	+0.36
3	$(CF_3)_2CCH{=}CHCH_3$	0.11±0.01	+0.28
4	$CF_3CF_2CF_2COO(CH_2)_3CH_3$	0.12±0.02	+0.37

It follows from the concentration dependence of the shifts that the transfer of the unpaired electron from oxygen to the organofluorine ligand and the paramagnetic shifts of the ^{19}F NMR peaks take place in equilibrium complexes and not in collision complexes; single-ligand complexes with a 1 : 1 stoichiometry of the interacting species, i.e. complexes of the type $M.O_2$, predominate under these conditions.

The equilibrium constants *K* for different molecules are fairly large and differ little from one another; in particular, they are almost identical (Fig.6) for the CF_3 and CF_2 groups of the molecules of compound 4 (Table 5). This constancy also indicates the localisation of the interaction of oxygen via the fluorine atom, in which the structure of the remainder of the molecule does not play an especially important role. Thus organofluorine molecules do indeed form fairly stable complexes with molecular oxygen in which the electron clouds of the interacting species overlap and there is a partial transfer of the unpaired electrons from oxygen to the ligand (the organofluorine molecule).

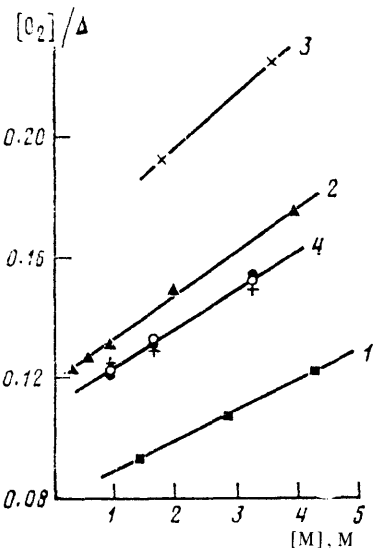


Figure 6. Concentration dependence of the paramagnetic shifts of the ^{19}F NMR peaks in terms of the variables of Eqn.(11); the numbers of the straight lines correspond to those of the compounds in Table 5.[24]

$K = 2.4 \times 10^{-2}$ litre mol^{-1} has been found reliably for *p*-difluorobenzene in benzene from the parameters of the ^{19}F NMR spectrum on the basis of the dependence of $\Delta^*(^{19}F)$ on the concentration of *p*-difluorobenzene (Eqn.11); $a(^{19}F)$ = +2.3 G. The ^{19}F peak shifts downfield, the shift being caused by the direct interaction of the π orbital of oxygen with the *n* orbital of the fluorine atom of the ligand.[16]

Signs of complex formation, namely the paramagnetic shifts of the peaks due to the ^{19}F and ^{13}C nuclei, have also been observed for a number of other organofluorine molecules.[25,26] We may note that no studies have been made of the concentration dependence of the shifts in the above investigations and the HFI constants calculated from the paramagnetic shifts in the pure, undiluted organofluorine liquids were therefore determined incorrectly. For this reason the correlations established by Hamza et al.[26] between the ^{19}F HFI constants

and the solubility of oxygen are erroneous and the conclusions based on these correlations concerning the causes of the high solubility of oxygen are unfounded.

Knowing the equilibrium constants, it is possible to calculate the fraction of oxygen bound in complexes in the solution.[24] Thus 52% of the entire dissolved oxygen is present in complexes in pure C_6F_6 at 40 °C, while in pure compound 2 (Table 5) 41% is bound under the same conditions; in compound 3 the proportion of oxygen bound in the complex with the CF_3 group is 37% and, when account is taken of all the fluorine-containing groups (CF_3 and CF_2), the proportion is 65%. We may note that the solubility of oxygen in organofluorine liquids exceeds on average its solubility in proton-containing analogues by a factor of 1.5–2. This "excess" oxygen content in organofluorine compounds is approximately consistent with the amount of oxygen incorporated in the complex, i.e. the cause of the anomalous solubility of oxygen in organofluorine compounds is its complex formation reaction.

V. OXYGEN COMPLEXES IN CHEMICAL REACTIONS

The question of the role of complexes in chemical reactions has no unambiguous solution; complex formation by no means always ensures the molecular organisation of the chemical reaction and frequently inactivates the reactants and inhibits the reactions.

Molecular oxygen is active in radical-chain reactions and its activity masks the chemical behaviour of its complexes. The contribution of chemical processes in which the complexes are detected or manifested can therefore be isolated only on rare occasions.

The photochemical oxidation of specially purified ethanol by molecular oxygen has been studied.[27] Solutions of oxygen in ethanol were irradiated with light corresponding to the absorption band, which appeared only in the presence of oxygen. It was found from the difference between the electronic absorption spectra of ethanol saturated with nitrogen and oxygen and was attributed to the oxygen complexes. This band lies in the range 2170–2700 Å and the intrinsic absorption of alcohol begins only at $\lambda < 2200$ Å. On irradiation with light at $\lambda > 2400$ Å, which is absorbed only by the complexes, oxygen was absorbed and oxidation products were formed. Both the kinetics of the consumption of oxygen and the composition of the products were typical for autocatalytic oxidation: the acceleration of the consumption of O_2 in time was observed and the yields of hydrogen peroxide and acetaldehyde (in comparable amounts) pass through a maximum, which is typical for intermediate products, while the yield of acetic acid (the final product) increased monotonically and reached a limit.

The oxidation was apparently initiated by the absorption of light by the oxygen complex (possibly with formation of the radicals $CH_3CH_2\dot{O}$ and $H\dot{O}_2$ or $CH_3\dot{C}HOH$ and $H\dot{O}_2$ as a result of the primary electron transfer in the excited complex and subsequent proton transfer). The disproportionation of the radicals in the primary pair can ensure comparable yields of CH_3CHO and H_2O_2 (as has been observed experimentally[27]). The subsequent consumption of these products cannot be accounted for unambiguously. It can be associated either with the fact that the oxidation is a chain process (possibly even with short chains) or the fact that oxygen also forms complexes with CH_3CHO and H_2O_2, which are involved in further photoinduced reactions. Experimental data do not so far permit unambiguous answers, but the conclusion that the complexes of O_2 with organic molecules initiate the photoinduced oxidation is entirely reliable.

The rules governing the autoxidation of organoelemental compounds also make it necessary to adopt the hypothesis of the formation of an oxygen complex as the first stage in the oxidation process. The presence of this stage has been justified experimentally in the oxidation of diethylcadmium;[28] the oxygen complex is transformed further into organoelemental peroxide compounds.

The behaviour of the O_2 + trimethylboron system has been subjected to a quantum-chemical analysis.[29] The geometrical parameters of the system and the orientation of the interacting species are illustrated in Fig.7. As the species approach one another to a distance $r \leq 3.5$ Å, their energetically favourable orientations are grouped near the C_3 symmetry axis of the trimethylboron molecule, i.e. oxygen tends to "stick" to the boron atom. As the O_2 molecule moves along the z axis on the potential energy surface, there is a local minimum corresponding to an intermediate complex in a triplet state (complex A), whose coordinates are $r = 2.25$ Å, $\gamma = 100°$, and $\alpha = 0$. It is subsequently transformed into another complex with the coordinates $r = 1.65$ Å, $\gamma = 102°$, and $\alpha = 90°$ in a triplet state (complex B).

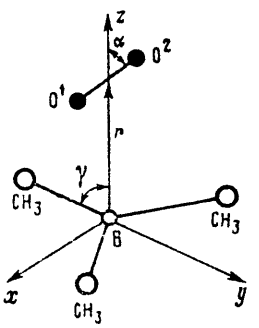


Figure 7. The geometrical parameters of the O_2 + trimethylboron system.[29]

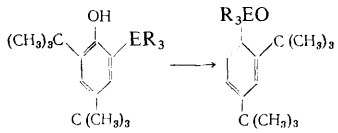
For the singlet state of the system, there is one minimum on the potential energy surface (whose coordinates are $r = 1.60$ Å, $\gamma = 102°$, and $\alpha = 90°$) and the transfer of complex B to this minimum hardly requires a change in energy and is accompanied by a redistribution of electron density.

On moving along the reaction coordinate, electron density is transferred from the O_2 molecule to the other species involved, the strength of the O–O bond in the O_2 molecule diminishes (mainly as a result of the loosening of the π-bond), and the B...O_2 bond formed has σ character. One of the B–CH_3 bonds is weakened and oxygen is inserted with formation of $(CH_3)_2BOOCH_3$. It has been suggested that the primary peroxides, whose subsequent decomposition initiates the chain oxidation of the organometallic compound, are formed via this pathway.

A minimum on the potential energy surface has also been predicted theoretically for the complexes of O_2 with benzene, pyrrole, and aniline, where O_2 is located above the plane of the molecules, the depth of the minimum being independent of the mutual orientations of the interacting species and the equilibrium distance at the minimum is approximately 3 Å, while the charge is transferred from the aromatic molecule to O_2.[30] It is difficult to say anything definite about the reliability of these results.

Finally one should note the influence of oxygen on the isomerisation of organoelemental phenols.[8] In the absence

of oxygen, shielded phenols (Table 1) are stable, but in the presence of O_2 they rearrange to ethers, for example:



;

E = Si, Ge .

Oxidation products are not then observed, which makes it necessary to assume that the rearrangement takes place in the complex of molecular O_2 with phenol. A correlation has actually been found between the stability of phenols with respect to the rearrangement and the complex formation constants K determined from the quenching of the luminescence (Table 1): the higher the value of K, the easier the rearrangement of the phenol.

The complex formation reaction with oxygen is probably important in the initiation of oxidation processes, especially in the atmosphere (in particular in the decomposition of Freons). Nor can one rule out the involvement of the complexes in steps where oxygen adds to radicals in kinetic chain propagation reactions.

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Many spectroscopic features (the removal of spin prohibitions, the appearance of new absorption bands, and the quenching of excited states) indicate the formation of complexes between molecular oxygen and organic molecules. However, the most reliable criteria and evidence for complex formation are the paramagnetic shifts of the NMR peaks and their temperature and concentration dependences. They demonstrate unambiguously that the formation of normal, equilibrium complexes constitutes the main and "strongest" intermolecular interaction in the oxygen–organic molecule pair. This is accompanied by the combination of the electron clouds of the interacting species and the partial transfer of unpaired electrons from oxygen to the ligand. The equilibrium constants and the fraction of spin density transferred have been determined for a number of organic molecules and even the energy has been estimated for some of them.

The n orbitals of oxygen (they give rise to complexes of the $n-\sigma$ type) and the π orbitals (giving rise to complexes of the $\pi-\sigma$, $\pi-n$, and $\pi-\pi$ types) participate in complex formation, the π-complexes predominating.

A number of examples indicating the involvement of the oxygen complexes in chemical reactions were examined above. However, one can assume that their importance in chemistry is much wider. The oxidation of polyconjugated aromatic molecules to endoperoxides and the oxidation of polyene hydrocarbons (β-carotene, retinal, and vitamin A) and polymers (polyacetylene) apparently proceeds via $\pi-\pi$ complexes. The oxygen $\pi-\sigma$ complexes lie on the coordinate of the RH + O_2 → $\dot{R}$ + $H\dot{O}_2$ reaction, which ensures the initial chain initiation in chain oxidation processes. Their role is also important in the photoinitiation of oxidation processes, because the complexes exhibit an intrinsic optical absorption. These processes are particularly significant in the chemistry of the atmosphere in connection with the danger of the breakdown of the ozone layer by Freons. The formation of complexes between Freons and oxygen and their photodissociation can prove to be important elements of the mechanism of the decomposition of Freons in the atmosphere and they must be taken into account in modelling chemical-ecological phenomena.

There is little doubt that elementary photophysical processes involving the oxygen-induced quenching of the excited states and sensitisation (deactivation, energy transfer, the removal of spin prohibitions, and the change in spin multiplicity) are induced precisely in the complexes and that the exchange-resonance mechanisms of these processes operate in the latter.

Finally, the formation of complexes by molecular oxygen has so far been only slightly investigated; there is little information about the structure and dynamics of the complexes, about their reactivity, and about their role in chemical reactions of oxygen. This applies particularly to the complexes of oxygen with organoelemental molecules, among which a special place belongs to the oxygen complexes of organofluorine derivatives. Much remains obscure and contradictory concerning the formation of complexes between oxygen and aromatic molecules and concerning the way in which the interacting species are "joined together" in the complex.

However, the considerable progress achieved in this field during the last three–five years must be noted: until then, nothing definite whatsoever was known about the oxygen complexes (apart from certain assumptions and guesses). This progress is due to the development of new ideas and approaches (in particular the application of nuclear magnetic resonance) for the solution of complex formation problems. It is evident that the ideas and approaches developed can be used also to investigate the complexes of oxygen with inorganic molecules, for the solution of the problems of the activation of oxygen, in the search for and synthesis of molecular oxygen transporting agents, etc.

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Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow