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Formation of Free Radicals from Molecular Complexes

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The Review summarises results from various branches of chemistry having as a common theme the part played by donor-acceptor molecular complexes in the generation of free radicals. Attention is paid mainly to liquid-phase reactions. One section deals with polymerisations involving molecular complexes. A list of 200 references is included.

CONTENTS

I.	Introduction	726
II.	Mechanisms of the formation of free radicals from molecular complexes	726
III.	Radical reactions involving molecular complexes in solution	730
IV.	Radical polymerisation involving complexes	733

I. INTRODUCTION

The theoretical importance of the formation of free radicals by the interaction of valency-saturated molecules was at one time pointed out by Semenov[1], but the experimental information which has been accumulated on this problem is still very limited[2]. Processes in which the appearance of radicals is preceded by preliminary donor–acceptor interaction of the molecules, leading to the formation of various types of complexes, have been better studied.

The importance of molecular complexes in chemistry is immense. During the twenty years that have elapsed since Mulliken worked out the principles of the modern theory of donor–acceptor interaction in complexes great progress has been made in elucidating the structure, geometry, and thermodynamic and spectral characteristics of the complexes. Detailed accounts of these topics are to be found in monographs[3,4]. Nevertheless, relatively few studies have been made of the part played by complexes in chemical reactions.

Reviews on the production of free radicals from complexes cover the literature up to 1963–1964.[5-7] In the present Review attention is paid mainly to various mechanisms by which free radicals are formed and to possible explanations of such processes in energetic terms. Use is made chiefly of results published during 1965–1970. Complexes formed by metal salts are not considered, nor are stable free radicals, aspects which have already been discussed in detail[8-11]. However, we have considered several papers in which free radicals were recorded and the existence of a complex can be inferred from the properties of the reactants.

II. MECHANISMS OF THE FORMATION OF FREE RADICALS FROM MOLECULAR COMPLEXES

1. Involvement of Complexes in Radical Reactions

Three tasks are involved in studying the part played by molecular complexes in the formation of free radicals: the existence of molecular complexes in the system must be proved, then free radicals must be detected or a radical reaction mechanism demonstrated, and finally a connection must be established between complex formation and the appearance of radicals. The last task is usually the most complicated.

Donor–acceptor interaction between reactant molecules changes their electronic structure and reactivity. Complex formation may be expected to increase the reaction velocity when interaction between donor and acceptor lowers the free energy of the transition state more than the energy of the ground state[12]. Such changes obviously occur in many biochemical processes, in particular in enzymic reactions, where the entropy factor plays a large part in the transition state[13]. The existence of molecular complexes can often be shown in the reactions of relatively small organic molecules, but it is not easy to prove that they are involved in forming the product[14]: the complex may be produced in parallel with the main reaction.

Let us examine the simple schemes of consecutive and parallel reactions

$$A + D \overset{K}{\rightleftarrows} \pi \xrightarrow{k_1} P, \qquad (I)$$

$$\pi \overset{K}{\rightleftarrows} A + D \xrightarrow{k_2} P, \qquad (II)$$

where A is an acceptor, D a donor, π the complex, and P the product. A choice between (I) and (II) cannot be based on the usual kinetic measurements[14,15]. Indeed, the low activation energy leads to rapid and reversible formation of a complex in solution at room temperature[14]. Rate constants for the formation and the dissociation of π–π complexes of 1,3,5-trinitrobenzene with deuterated fluorenes have been measured recently by quadrupole relaxation as respectively $(0.61–1.7) \times 10^{10}$ M^{-1} s^{-1} and $(0.53–1.5) \times 10^{10}$ s^{-1}.[16]

If a reaction occurs and a complex is formed in a system, and the latter can be monitored e.g. by means of its optical absorption, the disappearance of the complex in the system according to Eqn. (I) is described, for the normally chosen experimental conditions $[D]_0 \gg [A]_0$, by the equation

$$\ln\frac{[\pi]_0}{[\pi]} = \ln\frac{[A]_0}{[A]} = \frac{k_1 K [D]_0}{K[D]_0 + 1} t. \qquad (1)$$

If the complex coexists with formation of the final product [Eqn. (II)], we have

$$\ln\frac{[\pi]_0}{[\pi]} = \ln\frac{[A]_0}{[A]} = \frac{k_2 [D]_0}{K[D]_0 + 1} t. \qquad (2)$$

In both cases the reaction follows a first-order law, and the mechanisms cannot be distinguished[15].

Direct evidence of the formation of intermediate complexes has been obtained only for certain reactions in the gas phase[17].

With liquid-phase processes the problem of the participation of complexes in the reaction can be solved by a detailed study of the intermediate species. Correlations between various properties of the complexes and the reaction rate constants are also usually regarded as evidence of their involvement in the chemical process. Correlations have been observed between the reactivity of donor and acceptor and the stability of their complexes with substances which do not react with them [18]. The equilibrium constants of complex formation have been found to correspond with the rate constants in the interaction of a given acceptor with a series of donors [11,15]. A correlation exists between reactivity and changes in optical charge-transfer spectra [19].

A kinetic method, in which the reaction is conducted in different solvents, has also been proposed [20] for making a choice between schemes (I) and (II). The reaction of tetrachlorophthalic anhydride with triethylamine, which resembles the Menshutkin reaction and depends on the polarity and the polarisability of the solvent molecules, was investigated. The apparent first-order rate constant, determined experimentally from the decrease in the acceptor concentration, is connected with the equilibrium constant of complex formation and with the concentration of the donor, present in excess, by the relation $k_{exp} = k'[D]_0/(1 + K[D]_0)$. If the complex takes part in the reaction, we have $k' = k_1 K$. The values of k_1 and K can be obtained by reducing the above equation to the form [15,20]

$$1/k_{exp} = 1/k_1 + 1/k_1 K \cdot 1/[D]_0 . \qquad (3)$$

With parallel formation of the complex (scheme II) we have $k' = k_2$. If the rate constant of the Menshutkin reaction k^M is used to characterise the solvent, a definite regularity in the dependence of $\lg k_1$ on $\lg k^M$ should be observed if the complex takes part in the reaction. If, however, the complex is not involved in the reaction, a large scatter of the points should be obtained in the corresponding dependence of $\lg k_2$ on $\lg k^M$. On this basis it was concluded [20] that the charge-transfer complex is an intermediate product, and that the reaction occurs according to scheme (I).

Another approach to elucidating the part played by the complex in the reaction consists in lowering the temperature. This permits the study of intermediate products that are unstable at room temperature [21-23] and also diminishes the rate of all stages in schemes (I) and (II). With sufficient retardation of the most rapid stage of the reaction, an S-shaped rate curve representing accumulation of the reaction product may be observed experimentally if the product is formed from the complex (consecutive reaction). Here it is desirable that none of the elementary rate constants should differ too greatly in absolute magnitude. A negative temperature coefficient is also of interest: if the acceleration of the reaction when the temperature is lowered is associated with formation of an intermediate complex, this agrees with schemes (I)—not with (II). [15]

We have been discussing above the simplest consecutive and parallel reactions (schemes I and II). It is often suggested that two intermediate species, e.g. π- and σ-complexes [6,14], are involved in formation of the products. Thus for the scheme

$$A + D \overset{K}{\rightleftarrows} \pi \xrightarrow{k_3} R \xrightarrow[+D]{k_4} P \qquad (III)$$

(in which R is the second complex or free radical) the time variation in the concentration of the product P is expressed by the equation

$$[P] = \frac{k_3 k_4 [D]_0 [\pi]_0}{k_3 - k_4 [D]_0} \left[\frac{1 - e^{-k_4 [D]_0 t}}{k_4 [D]_0} - \frac{1 - e^{-k_3 t}}{k_3} \right] \qquad (4)$$

provided that $[D]_0 \gg [A]_0$ and with rapid equilibrium formation of π. In this case a sigmoid curve for the product can be observed comparatively easily. Fig. 1 shows theoretical rate curves for the accumulation of P with different ratios of k_3 to $k_4[D]$. [24] Schemes of type (III) should be found especially frequently with radical reactions, since the free radicals formed from the complex react readily with the starting materials to give the reaction products.

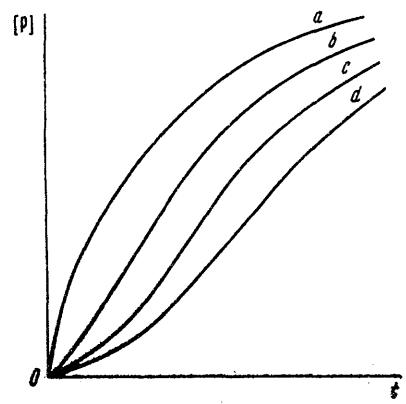


Figure 1. Theoretical rate curves for the accumulation of the reaction product according to: *a*) scheme (I); and according to scheme (III) with different values of $k_4[D]$: *b*) $8k_3$; *c*) $2k_3$; *d*) $1.2k_3$.

Evidence of the formation of the σ-complex from the π-complex—not directly from the original molecules—has been obtained from a spectrophotometric investigation of the reaction between N-substituted aromatic amines and chloranil in solution [22]. A kinetic study has been made of this process [23]. With low concentrations of donor and acceptor very little of the "external" (π) complex is present at room temperature, but it is observed on cooling to −80°C (the process is reversible). Formation of the "internal" (σ) complex in this case requires a further drop in temperature (to −196°C) in order to accumulate the π-complex, followed by a return to −80°C. When the π-complex is present in appreciable concentrations at room temperature, cooling to −80°C is sufficient for the σ-complex to be formed. Thus there exists a critical concentration of the π-complex necessary for further reaction [22]. A similar phenomenon is observed in several radical reactions involving an intermediate complex [25,26].

Formation of the same products by photoexcitation of the complex in the charge-transfer band as in the dark thermal reaction may be used as an argument that the complex is involved in the reaction even in the absence of illumination. This criterion has been applied, for example, to the reaction of acid chlorides with aromatic

amines[27] and to free-radical reactions involving tetranitromethane[25]. The formation of donor–acceptor complexes also favours photochemical reactions. Complex formation usually shifts the absorption maximum to longer wavelengths, and absorption may increase at a given wavelength. Thus complex formation has the effects firstly of increasing the efficiency of the absorption of light and secondly of permitting the use of irradiation with photons of lower energy and the avoidance of several side-reactions.

2. Possible Modes of Breakdown of the Complex into Radicals

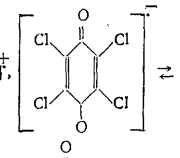
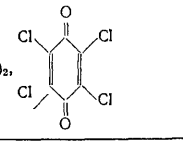
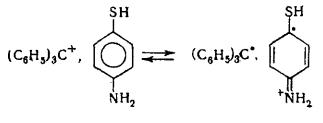
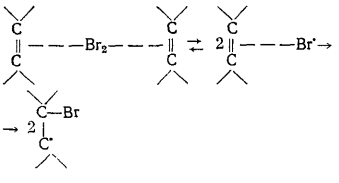
The wave function of a donor–acceptor complex in the ground state is given by a linear combination of wave functions of non-bonding and bonding configurations. There exist complexes with weak interaction, when the term describing a structure without charge transfer has the highest value in the wave function; and complexes with strong interaction, which are represented mainly by a structure with a transferred charge. In our opinion the nature of the ground state of the complex and of the radicals formed after charge transfer indicate that four main cases can be distinguished. These are given in Table 1 together with actual examples illustrating the general schemes.

Scheme 1. This shows that, if a complex consists in the ground state of two neutral molecules, an electron transition in the complex will lead to an excited state that is more polar than the ground state. In this case replacement of a less by a more polar solvent will shift the charge-transfer band to longer wavelengths. The effect is usually small, since solvent molecules require a finite time for reorientation around the polar excited state, while the ground state is only slightly solvated. Complete transfer of charge in such cases will yield two oppositely charged radicals.

Scheme 2a. In the ground state the complex consists of charged particles. Most complexes of this type that have been studied are pyridinium halides[6]. The position of the charge-transfer band in such complexes is strongly dependent on the polarity of the solvent. In polar solvents the ionic ground state is more strongly solvated than is the excited state, and this leads to a short-wavelength shift of the charge-transfer band. In this case complete transfer of an electron from donor to acceptor yields two uncharged radicals.

Scheme 2b. Free radicals are produced most easily in the case of complexes having strong interaction, when an electron is transferred spontaneously from the highest occupied orbital of the donor to the lowest vacant orbital of the acceptor. The radical pair thus formed can be regarded in some cases as a new ground state of the complex. When it is excited, charge transfer takes place in the opposite direction, and the excited state corresponds to the original structure[30]. Such cases are usually observed in solid crystalline paramagnetic complexes. Salts of radical-ions have been most thoroughly studied among solid-phase complexes. Such complexes have high electrical conductivity and are usually strongly paramagnetic[34]. Salts of radical-ions can be obtained both by the complete transfer of an electron from donor to acceptor and from "ready made" ions of the substances involved[35]. Such complexes show interesting behaviour in solution. In media of low polarity charge-transfer bands can be observed corresponding to the transfer of an electron from anion to cation. With increase in polarity of the solvent this band moves to shorter wavelengths[36], i.e. in the opposite direction to that for neutral complexes. The position of the charge-transfer band in such complexes corresponds to low energies, and can be observed in the infrared[30,36-40]. Assignment of the charge-transfer band may be made difficult by the absorption due to radical-ions. It should be noted that the ionic ground state of a complex in the solid phase is not necessarily preserved in solution. The electron spin resonance signal also frequently vanishes on passing into solution[41].

Table 1. Mechanisms and examples of the formation of free radicals from molecular complexes.

No.	Starting materials	Complex: gound state	Complex: excited state	Example	Ref.
1	A+D	(A, D)	$(\overline{A^{\cdot}}, \overset{+}{D^{\cdot}})$	$C_6H_5NH_2$, $(NC)_2C{=}C(CN)_2 \rightleftarrows [C_6H_5\dot{N}H_2]^{+\cdot}$, $[(NC)_2C{=}C(CN)_2]^{-\cdot}$	28
2a	$A^+ + D^-$	(A^+, D^-)	$(A^{\cdot}, D^{\cdot})$	$C_6H_5\overset{+}{N}CH_3I^- \rightleftarrows C_6H_5\dot{N}CH_3$, $I^{\cdot}$	29
2b	A + D	$(\overline{A^{\cdot}}, \overset{+}{D^{\cdot}})$	(A, D)	$[(CH_3)_2NC_6H_4N(CH_3)_2]^{+\cdot}$,  $\rightleftarrows (CH_3)_2NC_6H_4N(CH_3)_2$, 	30
3a	A + D^-	(A, D^-)	$(\overline{A^{\cdot}}, D^{\cdot})$	$C(NO_2)_4$, $C_6H_6O^- \rightleftarrows [C(NO_2)_4]^{-\cdot}$, $C_6H_5O^{\cdot}$	31
3b	$A^+ + D$	(A^+, D)	$(A^{\cdot}, \overset{+}{D^{\cdot}})$		32
4	D+X—Y	(D, X—Y)	(D, X˙ Y˙)		33

Spontaneous electron transfer usually occurs with donors of low ionisation potential I_D and acceptors of high electron affinity E_a. The best known donors, e.g. tertiary aromatic amines, have I_D = 6–7 eV. The electron affinity of such acceptors as tetracyanoethylene, tetracyanoquinodimethane, and chloranil is 2.4–2.6 eV according to the most recent results[42,43].

Schemes 3a and 3b. If the complex is formed by neutral and ionic components, one of the radicals will be neutral after electron transfer, and the other charged. Relatively few such examples are known[44].

Scheme 4. Cases are also possible in which one of the components of the complex breaks down into radicals in the course of complex formation, while the other remains unchanged, at least initially. Such a scheme corresponds formally to homolysis of the molecule as a consequence of its bonding into a complex, and will be examined in greater detail in Section III, 2.

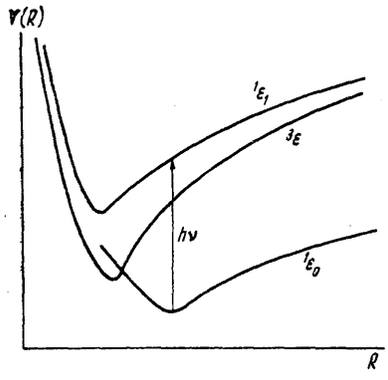


Figure 2. Potential-energy curves of ground and excited states of complex.

Study of the detailed mechanism of the formation of radicals from complexes has begun during recent years. Use is made mainly of the excitation of neutral molecules in the charge-transfer band combined with methods enabling short-lived intermediate species to be investigated. When the complex absorbs light of energy corresponding to the charge-transfer band and insufficient to excite the starting materials, it passes into the lowest excited singlet state (Fig. 2, curve $^1\epsilon_0$). This involves passage of an electron from a donor orbital to the lowest unoccupied orbital of the acceptor, while the total spin multiplicity is maintained. The electronic constitution and the structure of ground and excited states of the complex differ greatly. This leads to a considerable difference between the excited state formed in conformity with the Franck–Condon principle and the equilibrium excited state. As a result, mirror-image symmetry may not be satisfied between the absorption spectrum (i.e. the charge-transfer band) and the fluorescence spectrum [45]. The structure of the excited state of the complex is greatly influenced by the solvent. The excited complex is strongly polar, and the radical-ions formed may be stabilised in a medium of high dielectric constant. The whole process can be represented by the scheme

$$(D,\ A)_0 \xrightarrow{h\nu} (D^+,\ A^-)^*_S \xrightarrow{\text{solvent}} D^+_{\text{solvate}} + A^-_{\text{solvate}}\ .$$

If the complex does not dissociate, it is deactivated. The radiating transition to the ground state is registered as fluorescence of the complex:

$$(D^+,\ A^-)_S{}^* \longrightarrow (D,\ A)_0\ .$$

Intersystem conversion is possible with population of the lowest triplet level of one of the components of the complex, e.g. the donor:

$$(D^+,\ A^-)^* \longrightarrow (D_T{}^*,\ A).$$

Sometimes the lifetime of DT is shorter in the complex than in the free molecule. Its values for naphthalene and its trinitrobenzene complex, for example, are respectively 20 and 2 s:[46] i.e. typical quenching occurs. The quantum yields of the phosphorescence of aromatic molecules may be increased by the presence of donor–acceptor interaction. Since acceptor molecules do not usually contain heavy atoms, the increase in the spin–orbital interaction, which increases the probability of a singlet–triplet transition, obviously originates in the bonding of the donor into a complex[46,47]. This involves deformation of the molecular orbitals, mixing of s- and p-orbitals, and increase in the spin–orbital interaction. The relative arrangement of energy levels in the complex that is necessary for fluorescence to occur has been analysed[48].

Conversion from the lowest singlet excited state of the complex can theoretically produce a triplet state of the complex itself (Fig. 2, curve $^3\epsilon$). After this, phosphorescence of the complex becomes possible:

$$(D^+,\ A^-)^*_S \rightarrow (D^+,\ A^-)^*_T \rightarrow (D,\ A)_0.$$

Such a process is still the least studied, and interpretation of the experimental results is not always unambiguous.

Great progress has recently been made in the experimental detection of excited states in donor–acceptor complexes. When complexes of tetracyanobenzene and pyromellitic dianhydride with aromatic compounds were illuminated in the charge-transfer band with laser light of wavelength 3371 Å, the absorption spectrum of the undissociated complex in an excited singlet state could be recorded for a few tens of nanoseconds[49]. Excited states have been studied also by the laser photolysis of complexes of tetracyanobenzene with toluene in acetonitrile. The absorption spectrum of the species obtained by exposure to a ruby laser is closely similar to that of the radical-anion of the acceptor. Kinetic analysis has established that the photoinduced species are formed within 10 ns.[50] Fluorescence of the excited singlet complex in solution is observed comparatively rarely. It has been studied in complexes of acid anhydrides with aromatic compounds[51,52] and of tetracyanobenzene with toluene[53]. A systematic investigation[54] of the spectral characteristics of the complexes of tetrachlorophthalic and pyromellitic anhydrides with hexamethylbenzene involved study of the absorption and fluorescence spectra, together with determination of the quantum efficiency of fluorescence in various solvents at room temperature.

Detection of the triplet state of a complex was first reported in 1967, when complexes of tetracyanobenzene with aromatic compounds were illuminated in frozen solutions: both phosphorescence of the complexes in the triplet state[55] and their triplet electron spin resonance signal[56,57] were claimed to have been observed. However, it has since been shown[58,59] that the observed phosphorescence was due to a triplet excited state of the acceptor (tetracyanobenzene). The role of the triplet state of the complex in photoionisation has been studied also by low-temperature flash photolysis: this provided the first experimental detection of the spontaneous ionisation of the triplet state of the complex of pyromellitic dianhydride with mesitylene[60]. It was also concluded that the triplet state may be populated by direct excitation of the complex in the ground state.

Strong attraction between an excited ion-pair and a donor molecule may lead to association (formation of an eximer

$$D \cdots (D^+,\ A^-)^*_S.$$

After intersystem conversion, phosphorescence of the triplet eximer is observed [61]:

$$D - - - (D^{+\cdot}, A^{-\cdot})_S^{\cdot} \rightarrow (D, D_T^{\cdot}A) \rightarrow D + \cdot$$

With regard to the possibility of radical formation by thermal excitation of the complex, the lowest excited singlet state is energetically too high and is unattainable thermally. Theoretical examination of the energetics of complexes leads to the conclusion that, in the case of the uncharged ground state of the complex in systems comprising a donor of low ionisation potential and an acceptor having a positive electron affinity, the potential-energy curves of ground and triplet states of the complex may intersect [62,63]. If the point of intersection is sufficiently low energetically, thermal population of the triplet state of the complexes is possible (Fig. 2, passage from curve $^1\epsilon_0$ to curve $^3\epsilon$). In the case of a low-lying triplet state such electron transfer does not involve any considerable consumption of energy. Because of this, the thermal formation of radicals from molecular complexes can occur even when the charge-transfer band lies in the short-wavelength region.

III. RADICAL REACTIONS INVOLVING MOLECULAR COMPLEXES IN SOLUTION

Electron spin resonance can in many cases be conveniently used to demonstrate the radical nature of a reaction in solution. However, difficulties arise in assigning the e.s.r. signal to the complex itself. Formation of a triplet state, equivalent to a biradical, precedes the production of radicals by thermal or photoinduced electron transfer in the complex. After dissociation of the biradical, two e.s.r. spectra of equal intensity—due to donor and acceptor radicals—should both be present. Usually, however, only one radical is recorded in the e.s.r. spectrum after electron transfer in the complex and the formation of radical-ions [64]. This is probably due to dissociation of a radical-ion pair in solution into free radical-ions, one of which is more stable than the other. When e.s.r. spectra having a hyperfine structure are observed, they must evidently be assigned not to the complex but to radical electron-transfer reaction products; with a stable radical-ion pair, however, a wide signal should be observed, and at low temperatures the spectrum of the triplet state is registered [6]. The triplet state of a complex is in certain respects analogous to the radical pairs formed e.g. by solid-phase photolysis or radiolysis. The paramagnetism of such pairs has been studied quite thoroughly [65]. As already mentioned, the e.s.r. spectrum of the triplet state of a complex could be detected only in the solid phase. With regard to transitions having $\Delta m = 1$ and $\Delta m = 2$, exposure e.g. of complexes of tetracyanobenzene with methylated benzene derivatives at 77°K produces an e.s.r. signal in the region $g \simeq 4$. [56,57] An e.s.r. spectrum has been observed also in an analogous system on the irradiation of complexes placed in liquid crystals cooled to a vitreous state in a strong electric field. On excitation in the charge-transfer band, transitions were observed having $\Delta m = 1$ and $\Delta m = 2$. Each spectrum consisted of two groups of lines due to the triplet states of the donor and of the complex. This indicates the migration of energy from $(D, A)_T^*$ to D_T^*. The type of spectrum depends on the angle between the constant magnetic and electric fields; the method allows the orientation of complexes in the specimen to be studied [66]. The same paper reports observation of the e.s.r. spectrum of the triplet state of the complex in a tetracyanobenzene–naphthalene single crystal. At the same time both of the above transitions in the e.s.r. spectrum on the photochemical breakdown of the complex into radicals were detected also when the acridine–acridan system was illuminated in the charge-transfer band. Two types of radical pairs are formed in this system [67,68].

The use of electron spin resonance to investigate the radical reactions of complexes in solution is restricted by the low concentration and slow rates of conversion of complexes into radicals. The steady-state concentration of short-lived radical species in such reactions is often below the limit of sensitivity of the e.s.r. method.

1. Radicals with Electron Transfer from Donor to Acceptor in the Complex

In several cases increasing the polarity of the solvent does not produce the usual shift in the absorption band of neutral complexes in solution to lower frequencies, but a slight displacement in the opposite direction [69]. This effect is due to the influence of the solvent, which plays an extremely important part in reactions involving molecular complexes. Even in such solvents as hexane and carbon tetrachloride the reactant species which form the complex and the complex itself are in a state which is energetically greatly different from the gas phase [43,70]. The corresponding potential-energy curves will be found in Ref. 71, where the effect of the solvent on the thermodynamic characteristics of the complexes of tetracyanoethylene and iodine with several donors is discussed.

Dissociation of a neutral complex into radical-ions is facilitated by the lowering of the free energy of the latter state consequent on interaction with the solvent [72]. Solvation by a polar solvent makes dissociation into radical-ions energetically advantageous. If a complex is ionic in character in the ground state, a polar solvent tends to stabilise such state, and dissociation into radicals now occurs more easily in a non-polar solvent. This process can be represented as a chemical reaction involving the solvent S:

$$(D, A) + S \rightleftarrows D_S^{+\cdot} + A_S^{-\cdot} \,. \qquad (IV)$$

The equilibrium shifts to the right when the charge-transfer energy is less than the total energy of solvation of the two ions. The stability of the radical-ions towards recombination increases with the polarity of the solvent [73]. Thus it is important to know the energies of solvation of the species formed by dissociation in order to estimate the reactivity of complexes.

In solvents of low polarity the degree of charge transfer in most organic complexes, even those formed by strong donors and acceptors, is small. In polar solvents, however, ionic species may be formed. The reversibility of the process (IV) and the dependence of the position of equilibrium on the polarity of the solvent are supported by results reported in Ref. 74. The spectrum of an equimolecular mixture of tetramethyl-*p*-phenylenediamine and chloranil in acetonitrile exhibits bands corresponding to an anion (at 428 and 448 nm) and to a cation (568 and 618 nm) together with a band (843 nm) due to charge transfer in the complex. Addition of the non-polar carbon tetrachloride diminishes the absorption by the ionic species relative to that due to the complex. This change is reversible: addition of excess of acetonitrile again leads to a relatively greater intensity of absorption by the ions. Analogous results are obtained when the corresponding

ions—the perchlorate of the radical-cation of the amine (Wurster's salt) and the sodium salt of the radical-anion of chloranil—are taken as starting materials.

The effect of the solvent on a reaction may provide a definite criterion of a radical mechanism. With systems in which specific solvation is not of fundamental importance a weak solvent effect may indicate a reaction involving transfer of an atom, whereas a strong solvent effect usually indicates a reaction with transfer of an electron [75].

Electron spin resonance combined with ultraviolet spectroscopy will give a great deal of information on solvation effects in complexes. Taking the behaviour of the tetramethylhydrazine–iodine complex as example [76], we can divide the solvents investigated into three groups. In non-polar solvents (n-hexane, cyclohexane, carbon tetrachloride) there is no e.s.r. signal, but the ultraviolet spectrum contains a strong band due to the complex together with absorption by free and complexed iodine, the equilibrium constant being 450 ± 170 M^{-1} at 25°C. In solvents of intermediate polarity (chloroform, dichloromethane, isopropyl and isobutyl alcohols, dimethoxyethane) e.s.r. signals have already appeared with broad lines (1.7–4.4 G) due to the radical-cation of tetramethylhydrazine. In polar solvents (acetonitrile, acetone, methanol, water) fully resolved e.s.r. spectra are obtained with narrow lines (0.35 ± 0.03 G). In aqueous dioxan the e.s.r. spectral lines become narrower with increase in the radical concentration: i.e. the broadening is not due to spin–spin exchange, but results from electron exchange with tetramethylhydrazine not bound in the complex. The width of the e.s.r. spectral lines is constant in all polar solvents. In chloroform the e.s.r. signal slowly disappears, and the addition of polar solvents accelerates the destruction of radicals. No e.s.r. signal due to iodine is observed. When iodine is replaced by tetracyanoethylene the e.s.r. spectra of both radical-cation and radical-anion are observed in acetonitrile. From the results we arrive at the scheme

$$\begin{gathered}(CH_3)_2N{-}N(CH_3)_2 + I_2 \rightleftarrows (CH_3)_2N{-}N(CH_3)_2 \cdot I_2 \rightleftarrows \\ \rightleftarrows [(CH_3)_2N{-}\dot{N}(\overset{+}{C}H_3)_2\bar{I}\overline{\cdot}]_S \rightarrow \\ \rightarrow [(CH_3)_2N{-}N(CH_3)_2]_S^{+\cdot} + [I_2]_S^{-\cdot};\ [I_2]_S^{-\cdot} \rightarrow [I]_S^{\cdot} + I^-\end{gathered} \qquad (V)$$

In non-polar solvents the complex is undissociated. In solvents of moderate polarity the complex exists as solvated radical-ion pairs. In polar solvents the radicals are in the free form: the pairs are dissociated and the ions are solvated independently. The instability of the radical-anion of iodine makes the overall process irreversible.

Electron spin resonance spectra have been observed also in complex formation between iodine and tetraarylhydrazines in solution and in the solid state, each molecule of the complex being associated in the latter case with one unpaired electron [77]. Thus the e.s.r. method enables intermediate species to be studied in electron-transfer reactions, and free radical-ions to be distinguished from those combined in pairs.

Photochemical and kinetic studies provide valuable information on the mechanism of one-electron transfer in a complex with the formation of free radicals. When, for example, the tetracyanoethylene–oxolan complex was illuminated in its absorption band, the steady-state concentration of tetracyanoethylene radical-anions, with a characteristic nine-line spectrum, varied as the square root of the light intensity. The increase in the signal in the light was proportional to the square of the time, and the decay of the signal after the light had been switched off conformed to a second-order equation [78]. On the basis of the kinetic measurements it was suggested [78] that on the absorption of light the complex π is excited to a singlet state: $\pi \xrightarrow{I} \pi^S$, the rate of this process being proportional to the light intensity I. Transitions to the ground state $\pi^S \xrightarrow{k_2} \pi$ and to the triplet state $\pi^S \xrightarrow{k_3} \pi^T$ are unimolecular. However, the triplet state is converted into the ground state according to a first-order law: $\pi^T \xrightarrow{k_4} \pi$. If the singlet π^S had dissociated directly into radical-ions

$$\pi^S \longrightarrow D^+ + A^-,$$

solution of the corresponding kinetic equations would have led to a time dependence of the radical concentration involving a hyperbolic tangent. Such a relation was not observed experimentally. It was therefore concluded that the reaction proceeds through a triplet state:

$$\pi^T \xrightarrow{k_5} D^+ + A^-.$$

The most rapid among the various reactions of the radical-ions is recombination

$$D^+ + A^- \xrightarrow{k_6} \pi.$$

Solution of the kinetic equations with $[\pi^S]$ constant leads to direct proportionality between the observed steady-state concentration of radical-anions and the square root of the light intensity.

Photoinduced e.s.r. signals are detected in many complexes of acceptor molecules with donor solvents [79,80]. A more detailed study has been made of the chloranil–dioxan complex [79], on whose illumination the concentration of radicals reached its maximum value (10^{17} spins ml^{-1}) in 1–1.5 min, after which it decreased. This work is interesting also in the use of a rapid-response e.s.r. spectrometer (time constant ~ 0.03 s), in combination with a cumulative store to improve the signal noise ratio for the kinetic curves, in studying the kinetics of "rapid" e.s.r. signals (time to reach maximum concentration 0.1 s and time to die out after light switched off 0.05–0.15 s). The "rapid" e.s.r. signals are probably due to the primary products of photoexcitation of the complex. A more unambiguous interpretation is obtained in such cases e.g. by flash photolysis of the complex [29,60] or by investigations at low temperatures, when recombination of the radical-ions is much slower [80].

Electron transfer accompanying photolysis of a complex with formation of free radicals has been studied also in the reaction of amines with halogenated methanes [81] and with acid chlorides [27], oxolan with maleic anhydride [82], and ether with oxygen [83]. Detailed studies have been made of the low-temperature reactions of alcohols with halogens, which give radicals on photolysis of the unstable molecular complexes [84–86].

The spontaneous formation of radicals by thermal electron transfer in the complex is especially interesting. Thus on the dissolution of tetracyanoethylene in strong donors the e.s.r. signal of its radical-anions appears immediately, sometimes corresponding to up to 20% conversion of the original substance. An e.s.r. signal has been recorded on the dissolution of tetracyanoethylene in pyridine and its derivatives [87,88], in aromatic amines [28], dimethyl sulphoxide [73,89], *NN*-dimethylacetamide [73], and acetone [73,90], and also on its interaction with cyclopropylated ethylenes [91]. No e.s.r. signal appears in aprotic solvents [90], nor in the presence of oxygen [92]. The corresponding radical-cation is not usually observed, and the kinetics of the reaction can be followed conveniently

by means of the e.s.r. signal or the characteristic spectrum of the radical-anion of tetracyanoethylene in the ultraviolet and visible regions[28]. The formation of radicals depends on the polarity and the viscosity of the medium, since these factors influence the stabilisation of the resulting radical-ions and their rate of recombination[73,90]. In polar dimethyl sulphoxide, for example, tetracyanoethylene forms a strong 1 : 1 complex having an equilibrium constant of 95.4 ± 1.9 M^{-1} at 25°C and a heat of formation of $\Delta H = -11.3$ kcal $mole^{-1}$.[89] At low donor and acceptor concentrations the intensity of the e.s.r. signal is proportional to their concentration.

The following mechanism has been suggested for the formation of radicals[73]:

$$D + A \underset{k_2}{\overset{k_1}{\rightleftarrows}} \pi \underset{k_3}{\overset{k_2}{\rightleftarrows}} \pi^T \xrightarrow{k_4} D^+ + A^{\cdot-} \xrightarrow{k_5} \pi \ . \qquad \text{(VI)}$$

The complex is in a singlet ground state, but its formation involves partial thermal excitation to a triplet state. The singlet excited state is not formed, since it lies considerably above the ground state (3.34 eV); attempts to record fluorescence of the complex were unsuccessful. The triplet state either breaks down into radicals or returns to the ground state; the latter process involves a change in spin, and therefore occurs at a lower rate. With a large excess of the donor the recombination of radical-ions will also be a slow process. The absence of signals from the triplet state of the complex and from the radical-cation is explained by exchange broadening by collisions between π^T and π and also between $D^{\cdot+}$ and D.

The stability of the complexes formed by tetracyanoethylene varies in the sequence

dimethyl sulphoxide ($\Delta H = -11.3$ kcal $mole^{-1}$) > > *NN*-dimethylacetamide (−9.17) > acetone > > oxolan (−1.14).

In the first three solvents the formation of radical-anions is observed, a strong e.s.r. signal being obtained in dimethyl sulphoxide and dimethylacetamide ($[C_2(CN)_4^{\cdot-}] = 0.001$ M and $[C_2(CN)_4]_0 \simeq 0.0007$ M), in acetone the signal is weak, and in oxolan radicals are not detected. Thus a correlation exists between the stability of the complex, as measured by the change in enthalpy ΔH, and the e.s.r. signal. The high heat of formation of the complex with dimethyl sulphoxide displaces downwards all the levels in Fig. 3 due to the complex relative to the level of the free donor and acceptor molecules.

The triplet state of the complex is assumed to be populated thermally[73,89,90,92], which is confirmed by the proportionality of the e.s.r. signal intensity to $\exp(-\delta/kT)$. Calculation for the dimethyl sulphoxide complex with a Boltzmann distribution between the states (D + A) and $(D, A)^T$ gave $\delta \simeq 0.18$ eV and $J = 0.65$ eV, where $J = \delta + \Delta H$ is the singlet–triplet splitting. The corresponding energy diagrams for various solvents and a theoretical interpretation of the observed phenomena will be found in Refs. 73 and 89. According to the theory the rapid appearance of a dark e.s.r. signal is a general property of stable complexes. The signal intensity is closely connected with the heat of complex formation, which can thus be estimated. With ΔH determined by an independent method, the temperature dependence of the e.s.r. signal enables the activation energy δ to be found and hence J to be calculated. Because of the lack of convenient methods of measurement, the magnitude of this splitting is usually unknown for liquid-phase complexes.

Most complexes exhibit no electron spin resonance or else give only a very weak signal. In terms of the above scheme this is explained by the small heats of complex formation. The ground state of the complex is then close to the (D + A) level, and hence δ/kT is too large for appreciable thermal population of the $(D, A)^T$ level. It has been computed e.g. that the e.s.r. signal for the dimethyl sulphoxide–iodine complex ($\Delta H = -4.4$ kcal $mole^{-1}$) should be around 1% of that due to the dimethyl sulphoxide–tetracyanoethylene complex, and therefore is not observed.

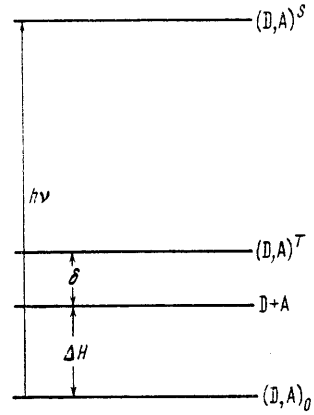
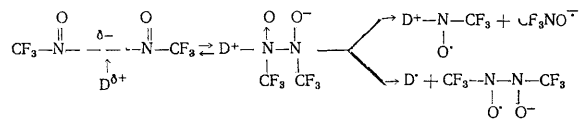


Figure 3. Energy diagram of various states of complex.

Thermal breakdown of a complex into radical-ions with transfer of an electron has been investigated in detail also in the reactions of nitroso-compounds with various electron donors[93–103]. The mechanism



(VII)

where D is a donor molecule, has been suggested e.g. for the dimer of trifluoronitrosomethane.

Electron transfer in a complex with the formation of radicals has been assumed also in the ozonisation of alkenes[104], the reaction of iodine with tertiary amines[105] and of tetranitromethane with tetra-alkyltetrazenes[106,107] and with 1,1-diphenylethylene[108], in the irradiation of the tetranitromethane–*N*-vinylcarbazole complex[26], and in the dissolution of chloroanil and benzoquinone in donor solvents[109]. An analogous mechanism of one-electron transfer in an intermediate complex probably operates in the reactions of peroxy-compounds with phosphites, sulphides, and aromatic amines. The kinetics and the mechanism of such processes have been discussed in a review[110]. The main part in the formation of peroxide complexes is played by hydrogen bonds[111]. Charge-transfer complexes may have an important role in biochemical processes[112]. Formation of free radicals from complexes takes place, for example, in the interaction of dihydroxyacetone with phenazine[113], of several medicinals (including antibiotics) with chloranil and other acceptors[114], and of flavins with phenols[115,116].

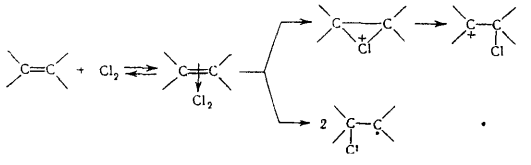
2. Radicals formed by Rupture of a Bond in One of the Components of the Complex

Free radicals are formed in several reactions of valency-saturated molecules at rates sometimes exceeding a hundredfold those calculated theoretically from the dissociation energy of the least stable bond. Such processes are sometimes termed *molecularly induced homolysis*, and their mechanism is not yet entirely clear [117,118]. In many cases such reactions have a radical-chain mechanism. A kind of feedback occurs in these processes: the energy required for dissociation of the molecule is partly or completely returned on the formation of new bonds after homolysis [2,119]. The solvent plays an important part in such reactions [120].

The formation of complexes in molecularly induced homolyses has been proved only in a series of reactions. In some cases their existence can be expected, since one of the reactants (often an alkene) has donor properties, while the other (e.g. a halogen) has acceptor properties. The formation of halogen–alkene complexes has been demonstrated experimentally [121,122].

Molecular complexes are probably involved in the formation of radicals in the liquid-phase chlorination of alkenes [119,123-128]. In the absence of light, oxygen, or a solvent the chlorination is a radical process with straight-chain alkenes and an ionic process with branched-chain alkenes. The radical reaction does not occur with tri- and tetra-alkylated alkenes. Oxygen strongly inhibits the radical reaction, which is then replaced by the slower ionic process. Dilution with a non-polar solvent also promotes the ionic reaction. Illumination increases the relative proportion of the radical reaction. The spontaneous formation of radicals in an alkene in the absence of a solvent and of oxygen is a rapid process unaffected by illumination. The reaction with cyclohexene goes readily even at -78°C. [119] The introduction of cyclohexane into the reacting mixture results in its chlorination, which proves the presence of chlorine atoms.

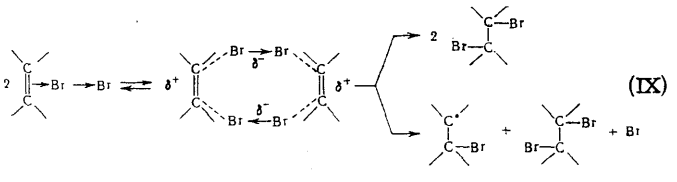
It is supposed that the reaction begins with the formation of an alkene–chlorine complex, which may either rearrange into ionic intermediate products or react with a second alkene molecule to form radicals:



(VIII)

Thus the classic scheme of the polar addition of chlorine to alkenes disregards all the specific features of the reaction. The low rate of initiation of free radicals is already sufficient for the radical-chain reaction to compete successfully with the ionic reaction [127].

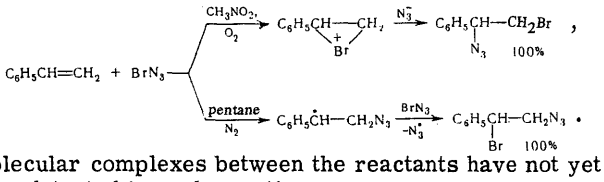
Schemes analogous to (VIII) have been suggested for the radical bromination [33] and nitration [86] of alkenes. A mechanism involving a complex containing two halogen molecules has been assumed [129] from kinetic results on the bromination of alkenes:



(IX)

Calculation shows that in this case the production of radicals is weakly endothermic ($q = -5$ kcal mole^{-1}), and therefore this mechanism has energetic advantages over the direct breakdown of a bromine molecule into atoms, which requires 46 kcal mole^{-1}. According to the above scheme polar and radical mechanisms of the halogenation of alkenes may involve closely similar transition states.

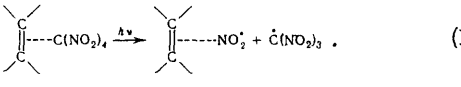
Complexes are probably involved also in the formation of radicals by the reaction of unsaturated compounds with iodine [130,131] alkyl hypohalites [120,132,133], halogen azides [134-137], peroxides [118], compounds containing a cyano-group [138], and ozone [104]. Spontaneous formation of radicals without initiation was observed in all these reactions. The possibility that molecular complexes are involved in directing the radical and ionic reactions is especially interesting. On the addition of bromine azide to alkenes, for example, theoretical yields of products of either the ionic or the radical reaction can be obtained depending on the conditions [135]. In the case of styrene, for example, the process can go according to the equations



(X)

Molecular complexes between the reactants have not yet been detected in such reactions.

The electronic rearrangement accompanying complex formation may tend to weaken a bond in one of the components [139]. In several cases the participation of complexes in the reaction is confirmed by combining photochemical decomposition with subsequent analysis of the resulting radicals by e.s.r. at low temperatures. In the photolysis of the complex of tetranitromethane with an alkene, for example, the energy of the quanta corresponding to the long-wavelength edge of the charge-transfer band is insufficient to rupture a bond in either component. In a mixture of the substances, however, tetranitromethane undergoes homolytic breakdown [25]. The latter is assumed to occur in conformity with the equation



(XI)

The free radicals formed by photolysis of the complex were identified by electron spin resonance at low temperatures. A similar reaction may occur even without illumination, obviously as a result of thermal excitation of the complex [140]. Under appropriate conditions the free radicals generated by the homolytic breakdown of tetranitromethane in the complex may lead to chain processes. The high quantum efficiency of the consumption of alkene and formation of a crystalline product on reaction with 1-phenylcyclohexene with illumination in the charge-transfer band, for example, indicates that the reaction has a chain mechanism [141].

Thus a detailed study of molecular complexes in such systems provides a deeper understanding of certain aspects of the mechanism of these reactions.

IV. RADICAL POLYMERISATION INVOLVING COMPLEXES

Many investigations have shown that a very promising method of polymerisation, besides the use of such

classical initiators as peroxides, diazo-compounds, etc., is the radical breakdown of molecular donor–acceptor complexes. Several facts indicate that complexes are involved in such reactions. Dilution of the reaction mixture with the solvent has been found to influence the composition of the polymer, a previously unknown effect. If the complex is responsible for the formation of a regular copolymer in the system, a diminution in this regularity is to be expected on dilution, which lowers the relative concentration of the complex. In the copolymerisation of divinyl ether with fumaronitrile, for example, dilution not only decreases the rate of polymerisation but also lowers the nitrile content of the copolymer [142].

If polymerisation takes place under the influence of active species formed by slow breakdown of a complex (e.g. according to scheme III), sigmoid kinetic curves should be obtained for the accumulation of the reaction product, as already mentioned. Such curves have been observed in several cases [143,144]. Finally, formation of a polymer having mainly a *cis*-1,4-microstructure by the interaction of butadiene with maleic anhydride confirms the involvement of a complex in the polymerisation [9,145]. The usual radical polymerisation of butadiene yields mainly the *trans*-1,4-microstructure. Thus the complexed diene—not the free compound—evidently takes part in the reaction, since precisely in the complex the strongest interaction with charge transfer should occur with a monomer having a *cis*-structure [145].

Complexes have a dual role in radical polymerisation: they are able firstly to initiate the reaction by breaking down into free radicals, and secondly to take part in chain growth by the bonding of free radicals into the complex. The Review considers mainly the process of initiation. The second aspect is also very interesting from both theoretical and practical points of view. The medium greatly affects the properties of free radicals, and solvation or bonding of the free radical into a complex may in considerable measure determine its reactivity in solution [8,11,146,147].

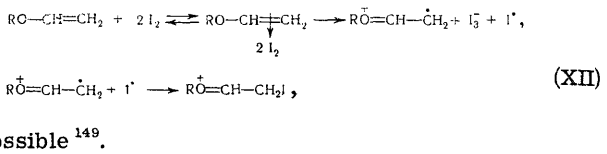
Examination of the literature reveals the following features of polymerisation initiated by molecular complexes. Such a reaction may occur at an extremely high rate, not attained with the usual initiators [148]. In some cases regular copolymers are formed, with a regular alternation of monomer units; independently of the proportions of the reactants, a 1 : 1 copolymer is usually obtained. The reaction mechanism cannot be described in terms of the laws of normal radical polymerisation. Sometimes the complex formed by the starting materials can be regarded as a monomer that is considerably more reactive than the usual monomers. Cases have been described in which neither component monomer of the complex is capable of polymerisation even in the presence of a radical initiator, whereas a mixture of the monomers is easily copolymerised even in the absence of an initiator [149]. On the other hand, the formation of a stable complex may so inactivate the monomer that polymerisation does not occur even in the presence of a radical initiator [150].

All cases of polymerisation initiated by the breakdown of a molecular complex into radicals can be divided into two groups. The complex may be a foreign reagent with respect to the monomers: i.e. its function is identical with that of the usual radical initiators. On the other hand, the initiating complex may include one or more monomer molecules. In the latter case the composition of the polymers can be varied by changing that of the complex, e.g. by the addition of various complexing agents [151,152].

The specific features of polymerisation initiated by a complex are due to the formation by electron transfer of two radical-ions

$$(A,\ D) \rightarrow A^{\cdot-} + D^{\cdot+},$$

which have different destinies. The ions may recombine, when it is supposed that polymerisation is begun by a biradical [148,153]. Recombination of the radicals yields a dipolar zwitterion $^{-}A-D^{+}$, which initiates ionic polymerisation [153]. Recombination of the radical centres may occur as a result of various secondary processes [143,149]. In the ionic polymerisation of vinyl ethers in the presence of iodine, for example, the reactions



(XII)

are possible [149].

Thus ionic and radical mechanism are closely connected, which explains the influence on radical polymerisation exerted by inhibitors of the ionic reaction [154]. When radical-ions are formed, ionic polymerisation is possible; this may be greatly accelerated by light, which facilitates electron transfer in the complex [155–157]. The mechanism of the conversion of radical-ions into carbonium ions has not yet been finally elucidated [158,159]. When one or both radical-ions obtained from the complex react with monomer molecules, the addition of the very first monomer molecule leads to the separation of ionic and radical centres, and here also both ionic and radical polymerisation is theoretically possible [153].

By no means all the above mechanisms are realised in practice. Thus the monomeric radical-cations studied hitherto do not exhibit simultaneous cationic and free-radical activity during polymerisation; no examples have yet been found of the formation from $D^{\cdot+}$ of bications $^{+}D-D^{+}$ to lengthen the chain. Many electron acceptors present in a complex are inhibitors of free-radical reactions, and perhaps suppress the radical activity of $D^{\cdot+}$. [149]

The dissociation of weak complexes into radicals cannot be detected experimentally by electron spin resonance, but the concentration of radicals is nevertheless sufficient for polymerisation to occur [160]. Examination of the kinetics of polymerisation is then a convenient method for studying the rate of breakdown of the initiating complex. In many cases in which the complex served merely to generate radicals, for example, the reaction velocity was proportional to the square root of the concentration of the complex [161–164]. The simplest explanation of this relation is the formation of an equilibrium complex, whose consumption is accompanied by the appearance of free radicals that react with the monomer [161]. More complicated mechanisms have also been suggested [163,165].

The most detailed study has been made of the initiation of polymerisation by complexes of aromatic amines with carboxylic acids and their derivatives. A relation has been established between the energetics of formation of the complexes and the kinetic parameters of the polymerisation initiated by them. The results are presented in Table 2.

The reactions between amines and acid chlorides are rapid. With an initial concentration of 0.1 M, for example, the half-conversion time is of the order of milliseconds [167]. A low-temperature technique is used [168] to study such complexes and their reactions. Bands due to complexes of anhydrides with amines have been detected at −196°C.

When the temperature rises by a few tens of degrees, chemical reaction occurs with disappearance of the complex. The infrared spectra indicate a decrease in the concentration of anhydride and amine groups, together with the formation at low temperatures of an ammonium salt [168].

Table 2. Influence of reaction conditions on the activation energy E_a for the polymerisation of methyl methacrylate initiated by the complexes of dimethylaniline with various acceptors.

Acceptor*	Parameters of complex			E_a, kcal mole^{-1}				Ref.
				no solvent		in acetonitrile		
	$h\nu_{max}$, kcal mole^{-1}	K_{eq} (25°C)	$-\Delta H$, kcal mole^{-1}	dark reaction	photochemical reaction	dark reaction	photochemical reaction	
TCPA	62.3	10.85	3.6	—	—	7.2	—	164
PA	76.2	4	2.0	—	12.0	11.5	11.5	164, 166
IPC	79.5	6.65	1.8	—	—	8.8	—	164
BAn	84.5	3.51	1.2	—	13.2	11.0	11.0	164, 165
BC	84.6	9.5	1.1	13.5	—	7.0	—	162, 164
BAc	—	—	—	13.2	6.4	—	—	161

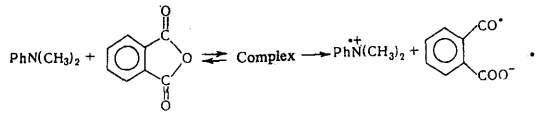
*TCPA = tetrachlorophthalic anhydride
PA = phthalic anhydride
IPC = isophthaloyl chloride
BAn = benzoic anhydride
BC = benzoyl chloride
BAc = benzoic acid

The following schemes have been suggested for the formation of radicals by electron transfer in complexes of aromatic amines [161,169]:

$$PhN(CH_3)_2 + PhCOOH \rightleftarrows Complex \longrightarrow Ph\overset{\cdot+}{N}(CH_3)_2 + PhCO^{\cdot} + OH^-,$$

$$PhN(CH_3)_2 + PhCOCl \rightleftarrows Complex \longrightarrow Ph\overset{\cdot+}{N}(CH_3)_2 + PhCO^{\cdot} + Cl^-,$$

$$PhN(CH_3)_2 + (PhCO)_2O \rightleftarrows Complex \longrightarrow Ph\overset{\cdot+}{N}(CH_3)_2 + PhCO^{\cdot} + PhCOO^-,$$



Breakdown of the complex is facilitated by ionic solvation, the effect being most strongly developed when the chloride ion is formed, and weakest with the radical-anion from phthalic anhydride. With strong complexes in a polar solvent it is sometimes possible to record the e.s.r. spectrum of the radical-cation of the amine [170,171]. However, it has been shown that polymerisation is initiated by the hydrocarbon radicals [172]. The rate of breakdown of the complex is strongly affected by light and the presence of oxygen, as well as the polarity of the medium [160,170,171,173-175].

As well as the complexes of amines with acid derivatives, polymerisation has been initiated by the use of complexes of nitrogen heterocycles with sulphur dioxide and with halogenated methanes [150], complexes of polymers with sulphur dioxide and carbon tetrachloride [150,185], and previously illuminated complexes of maleic anhydride with amides [176-178] and oxolan [179,180].

The mechanism of polymerisation initiated by complexes containing monomers has not yet been finally elucidated. Several authors hold the view that the determining factor is radical–monomer interaction in the transition state: others consider that the formation of copolymers of alternating structure is due to the involvement of molecular donor–acceptor complexes in initiation and chain growth [9]. Only one monomer—the donor—can enter the complex, and the second component is then an acceptor of electrons [149,181]. It is usually supposed that such a mechanism applies e.g. to the polymerisation of *N*-vinylindole and *N*-vinylpyrrole under the influence of chloranil, tetracyanoethylene, and other acceptors [182], and also the polymerisation of *N*-vinylcarbazole in the presence of chloranil and tetranitromethane [143,183]. In some cases initiation has been effected by illuminating the complex in the charge-transfer band [184].

The complex may also consist of two monomers, one with donor properties and the other with acceptor properties. Examples of reactions of this type that have been investigated are the copolymerisation of dioxen with maleic anhydride [185-187], of 1,2-dimethoxyethylene with maleic anhydride [187], of styrene and butyl vinyl ether with maleic anhydride [188], of butyl vinyl ether with acrylonitrile and maleic anhydride [189,190], of methyl methacrylate with the dimer of methyl vinyl ketone [191] and with *N*-vinylpyrrolidone [192], and also of sulphur dioxide with several olefinic compounds—1-methylcyclopropene [144], cyclopentene [193], bicyclo[2,2,1]hept-2-ene [148], styrene, and methyl methacrylate [194].

The possibility of polymerisation with weak complexes, incapable of complete electron transfer with dissociation into radicals, is explained on the assumption of mutual activation of donor and acceptor in the complex [149].

Valuable information on the reactivity of the complex is obtained from a study of ternary copolymerisation. In several cases the reaction in which donor and acceptor monomers enter the polymer chain alternately can be regarded as the binary copolymerisation of the complex formed by these monomers with a molecule of the third monomer [195]. Ternary copolymerisation has been studied on the systems

styrene–maleic anhydride–sulphur dioxide [151]
2-chloroethyl vinyl ether–maleic anhydride–acrylonitrile, dioxen [145,196,197]
methyl methacrylate–methyl vinyl ketone dimer–styrene, acrylonitrile [191]
methyl methacrylate–maleic anhydride–*N*-vinylpyrrolidone [198]
cyclopropene–acrylonitrile–sulphur dioxide [199]
dioxen–maleic anhydride–2-chloroethyl acrylate [200]
anethole–maleic anhydride–2-chloroethyl methacrylate, methacrylonitrile, acrylonitrile [195]

in the last three of which a kinetic study was made.

An interesting investigation has recently been made of the relation between the thermodynamic constants of the complexes formed by two monomers in various solvents and the reactivity of these complexes [197]. Increase in the equilibrium constant of the complex as the solvent is changed leads to an increase in the reaction velocity. When different complexes are compared, however, the main factor is not the concentration but their reactivity. For example, 1,4-dioxen and 2-chloroethyl vinyl ether become more reactive by factors of 31 and 11 respectively when they enter a complex with maleic anhydride. The same paper proposes a classification according to which all polymerisation reactions involving complexes are divided into several classes according to the equilibrium constant K_{eq} of the complex. When $K_{eq} \simeq 0.01$, reaction either does not take place at all or occurs only in the presence of an initiator. When K_{eq} increases to 0.1–1, the radical or

ionic reaction may occur spontaneously. A stable complex ($K_{eq} \to \infty$) is unable to initiate polymerisation.

Thus the above results indicate the wide possibilities for varying the rate and the selectivity of polymerisation processes and the structure of the polymers by combining the initial monomers into complexes.

Examination of the literature thus reveals only a small number of investigations, based on kinetic results, of the conversion of molecular complexes into free radicals. The mechanism of the process, especially in the absence of light, is still obscure. Rearrangement of the electronic structure accompanying complex formation may obviously weaken a bond in one of the components. In several cases a correlation has been established between the e.s.r. signal and the enthalpy of formation of the complex. Investigation of the entropy contributions in such processes is extremely important.

The high rate and the reversibility of complex formation often lead to ambiguity in the kinetic results. Processing the experimental data on electronic computers would enable the reliability of the proposed mechanisms to be assessed.

Fresh correlations must be sought between the thermodynamic characteristics of complex formation (K_{eq}, ΔH, ΔS) and the reactivity of the molecular complexes. In our view, a promising line of research would be the kinetic investigation of systems in which several complexing processes are competing (e.g. the interaction of reactant molecules with themselves and the solvent). Knowledge of the energies of solvation of the species formed from the complex would facilitate a quantitative estimate of the reactivity of the complexes. Such data could usefully be obtained by means of nuclear magnetic resonance, a method which in several cases gives reliable information also on the thermodynamic characteristics of molecular complexes. Thus the most effective way of solving the problem discussed in the Review, is to combine various methods of investigation (kinetic, photochemistry, in particular flash, e.s.r., and n.m.r.). When analysing the mechanism of the formation of radicals from valency-saturated molecules, we must take into account the possibility of competition between the appearance of radicals by electron transfer in the complex and directly from the original molecules under the influence of the solvent.

Examination of the role of molecular complexes in the formation of free radicals, especially in the case of polymerisation processes, shows that radical and ionic mechanisms are more closely connected than had been assumed. This connection is understandable if the initial stage is electron transfer in the molecular complex with the formation of radical-ions. Study of the laws of the conversion of molecular complexes into other active intermediate products will permit control of the rate and the selectivity of the most diverse processes.

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