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KINETICS OF RADICAL POLYMERIZATION—XVII

THE EFFECTS OF CHARGE-TRANSFER COMPLEXES ON SOME ELEMENTARY PROCESSES IN RADICAL POLYMERIZATION

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Abstract—The molecular compounds (charge-transfer complexes) which may be formed in some radical polymerizations influence greatly the kinetics of the processes. We have investigated theoretically those factors which determine the parameters of the reactions between radicals and their reaction partners with a closed shell π-electron system. Special attention has been paid to the effect of the formation of molecular compounds. We have concluded that the increase of reactivity can be attributed to the increase in the resonance energy of the transition state. On this basis, some anomalous effects in inhibited polymerizations and in copolymerizations can be satisfactorily interpreted.

1. INTRODUCTION

The interest devoted to a class of organic molecular compounds, viz. the group of charge-transfer complexes (π-complexes, EDA-complexes) has considerably increased in the last decade. The most important result in this field was the satisfactory quantum chemical interpretation of the characteristic spectroscopic features of these molecular compounds.(1,2)

Investigations have shown that, for organic compounds having a π-electron system, charge-transfer complexes may be formed if one molecule has electron-donor properties and another has electron-acceptor properties. Such molecular compounds may have a role in certain chemical processes. This belief was accepted first in biochemistry,(3) but no unambiguous results have been achieved so far.

The effect of the formation of molecular compounds upon elementary chemical reactions can be considered as fully clarified, however, in some radical processes, e.g. the radical polymerization of styrene.(4) If an inhibitor or a co-monomer possesses electron-acceptor properties, then it will form with the electron-donor styrene monomer an easily demonstrable molecular compound; the kinetics of the relevant reactions are likely to be affected profoundly. So, for instance, in the polymerization of styrene inhibited by picric acid,(5) the reactivity of the latter decreases rapidly with decrease in the concentration of styrene. An analogous phenomenon, due to a decrease in the relative concentration of the monomer–inhibitor complex, can be observed also in the case of the halogen-substituted quinones. Similarly the fact that in the alkyl-substituted quinones (where the formation of molecular compounds is insignificant) the reactivity is a linear function of the redox potential, while halogen-substituted quinones show considerable positive deviations, finds its explanation also in the formation of molecular compounds.(5)

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2. REACTION OF RADICALS WITH π-ELECTRON SYSTEMS HAVING A CLOSED SHELL

Under the usual conditions of radical polymerization, the reaction between radicals and molecules with closed shell π-electron systems are generally characterized by a small activation energy (about 2 or 3 kcal/mole) and by a surprisingly low (10^2–10^6) pre-exponential factor.(7–9) In these reactions, it is not the activation energy but the transmission coefficient ($\ll 1$) which determines the reactivity. It is a common feature of these reactions that they modify the total π-electron energy of the system to a great extent, either increasing or decreasing it. For interpretation of this general phenomenon, consider the effect of the distance between the two reaction centres.

If the bond distance R—Z is finite, and if a chemical interaction occurs between the two reacting substances, it seems advisable to examine the complete system instead of molecule Z alone. In Fig. 1 the conditions are represented in accordance with this.

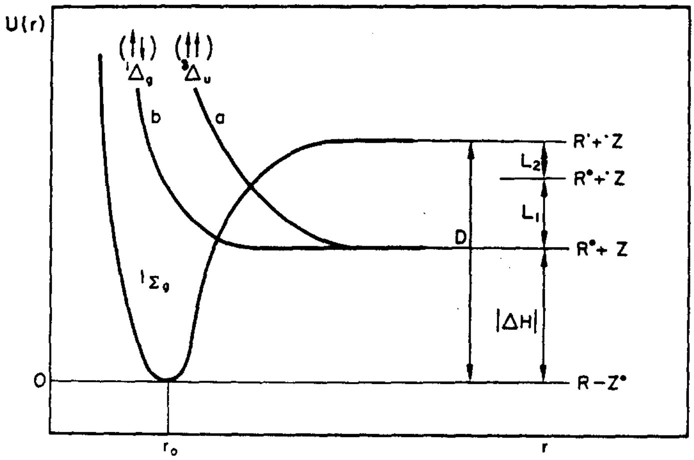

FIG. 1. Potential curves of the radical + molecule system (i.e. of the total energy as a function of the relative distance) D = dissociation energy of bond R—Z$^{\cdot}$, L_1 and L_2 = the localization energy of the π-electron of the molecule or of the radical respectively.

The energy levels corresponding to the different electronic states are indicated; localized electrons are indicated by small and delocalized by large dots.

The state of the two electrons of the newly formed σ-bond in the reaction is $^1\Sigma_g$. During the approach of the reaction partners, two different positions may be taken up by the π-electron of the radical, corresponding either to parallel or to anti-parallel spin, relative to the π-electron successively becoming localized at the reaction centre. In these cases, the state of these two electrons, taking into account also the multiplicity, is either $^3\Delta_u$ (curve a) or $^1\Delta_g$ (curve b). Along curve a, considerable repulsion arises while along curve b the repulsion is insignificant.

The reaction occurs at one of the intersection points. The transitions $g \rightarrow g$ (and $u \rightarrow u$) being strictly forbidden, the reaction should occur according to the allowed $u \rightarrow g$ transition. This reaction requires considerable activation energy.

A second way of reaction (transition $g \rightarrow g$) although forbidden, cannot be completely excluded. If the wave function of the π-electron of the attacking radical or of the inhibitor molecule has a certain s character, this transition becomes less strictly forbidden and therefore there is a small probability for this reaction path. For interpretation of the hyperfine splittings observed for many radicals studied by E.S.R., a slight s character for the unpaired electron must be assumed.(10) On the basis of the kinetic parameters for reactions of this type and of the above considerations, it seems more probable that the reaction follows the latter non-adiabatic path.

Consider now the regions near the points of intersection of the potential curves (see Fig. 2).

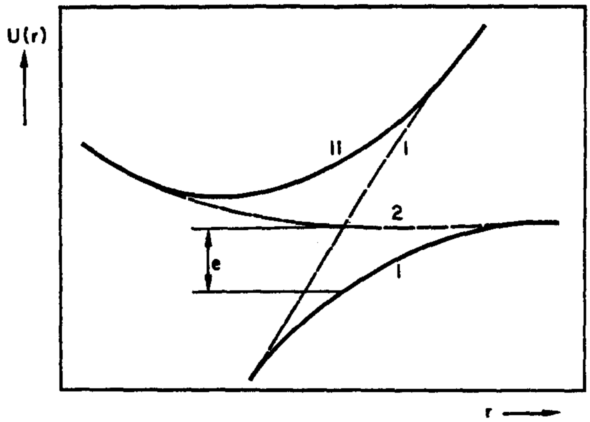

FIG. 2. The neighbourhood of the point of intersection of the potential curves. e = the resonance energy in the transition state.

In this representation, the movement on the same potential surface (or in the two-dimensional case on the same potential curve; curves I or II) corresponds to the adiabatic movement. If, however, the movement does not occur on the same potential surface (i.e. along curve 1 or 2) and there is transition of the system from one potential surface to another, the movement will not be adiabatic.(11)

A number of non-adiabatic elementary reactions are known in addition to the usual adiabatic elementary processes. In these reactions, the transmission coefficient depends on the probability with which the system moves from one potential surface to the other. This probability has to be determined for the theoretical calculation of the reaction rate. The probability (P) for a non-adiabatic transition, as Landau(12) and Zener(13) have shown, is given by

$$P = \exp \{ -4 \pi^2 e^2/h v \mid F_1 - F_2 \mid \}, \tag{1}$$

where v denotes the relative rate of the particles, F_1 and F_2 the slopes of the potential curves at the point of intersection. Non-adiabatic transitions are evidently favoured by high relative rates, by a small value of the resonance energy e, and by a large difference between the slopes of the potential curves. For this reason, curves 1 and 2 are usually called "rapid" curves and curves I and II are referred to as "slow". If the particles are approaching or receding at great speed, there is no time for the re-arrangement of the π-electron system; thus its potential energy will be described by curves 1 or 2, i.e. the system moves from potential surface I onto II. On the other hand, in the case of a slow approach, an electron re-arrangement takes place and thus the system moves along curve I.

The following points should be noted in connection with the quantities appearing in Eqn. (1). The rate v is usually of the order of the rate of thermal motion unless particles of particularly great kinetic energy are involved. The value of F_1 can be obtained from the Morse-function and that of F_2 by differentiation of the equation describing the van der Waals interaction between saturated molecules. If the activation energy is insignificant, as in the present case, the repulsion curve can be supposed to intersect the attraction curve horizontally so that $F_2 = 0$. In this case, the observed activation energy of $\sim$ 1·5–3 kcal may be considered as translational energy from which, knowing the molecular weight, v can be calculated.

Calculation of the resonance energy e is the most problem. According to quantum mechanics

$$e = \int \psi_1 \, H \, \psi_2 \, \mathrm{d}v, \tag{2}$$

where ψ_1 is the eigenfunction of the initial state and ψ_2 is that of the final state of the system, while H is the perturbation Hamiltonian. It is easy to show that in the general case the value of this integral is not zero, so that the potential surfaces do not intersect (see curves I and II in Fig. 2). The cases in which the functions ψ_1 and ψ_2 have different symmetries are exceptions to the above rule, the value of integral (2) being zero for all internuclear distances. A minor interaction can occur also in these cases (e.g. a spin–orbit interaction); this is, however, smaller by several orders of magnitude than the usual values of the perturbation energy (10^{-4} to 10^{-5} eV compared with about 0·1 eV).(14) Thus in these cases, the potential surfaces do not intersect although they come very close to each other. In these cases, the probability of the non-adiabatic transition is close to 1, as is apparent from Eqn. (1). In such case, the representative point moves along curve 2 (elastic collision) and its transition to curve 1 (signifying the occurrence of reaction) occurs very rarely. It should be stressed that the "non-adiabatic" reactions are, in fact, adiabatic processes also, corresponding to movements on the lower potential curve (I) but the probability of this is very low. The elastic collision is the proper non-adiabatic process, as it is in this case that the representative point will be transferred from the lower to the higher potential surface. Another definition given for the adiabatic reaction is based on the symmetry properties of ψ_1 and ψ_2. According to this definition, a process is to be considered as adiabatic if the electrons taking part in the reaction can be described from their initial state through to their final state by wave functions of the same symmetry. From a practical point of view, it is the extreme smallness of the pre-exponential factor which is the most reliable criterion of non-adiabaticity with the exception of those cases in which an exceptionally great decrease of the activation entropy might be expected (as for example in a cyclic transition complex). Generally, however, identification of such cases is not difficult.

The transmission coefficient of the reaction (x) can be expressed by the probability of the non-adiabatic transition

$$x = 2\,P\,(1 - P). \tag{3}$$

This expression reaches a maximum at $P = \frac{1}{2}$, i.e. $x = \frac{1}{2}$. The relation $x = f(P)$ is shown in Fig. 3 where $X = 4\,\pi^2\,e^2/hv \mid F_1 - F_2 \mid$. For values of P of about 1, the expression simplifies to

$$x = 2\,(1 - P). \tag{4}$$

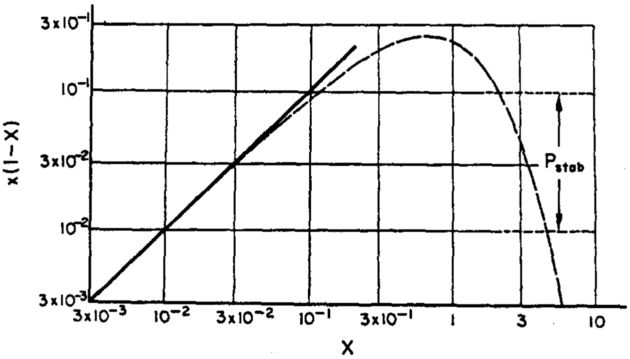

FIG. 3. Variation of the transmission coefficient as a function of X.

If P is much less than 1

$$x = 2P. \tag{5}$$

In the last case, the value of x is in fact determined by P_{stab} (the probability for collision stabilization) rather than by P. In such cases, almost every collision results in reaction but its energy-rich end-product immediately falls into fragments in the next vibration unless the heat of reaction is absorbed by some collision partner. For more complex molecules, it is even sufficient if part of the surplus energy passes from the degree of freedom of the reaction to another degree of freedom; this last case has, however, no practical importance for the systems to be examined here.

If a series expansion of (1) is used, expression (4) can be put into the form

$$x = 2X = 8\,\pi^2\, e^2/hv \mid F_1 \mid \tag{6}$$

using the condition that F_2 is zero.

In non-adiabatic reactions, the transmission coefficient can depend slightly upon the heat of reaction. If the potential curve of the radical R—Z can be described by the Morse-function, then at the point of the pseudo-intersection of the attraction and repulsion curves $U(r^+) = \mid \Delta H \mid$ so that the co-ordinate of the intersection will be

$$r^+ = r_0 - \frac{1}{a} \log \{1 - (\sqrt{\mid \Delta H \mid/D})\}. \tag{7}$$

The slope of the potential function at this point is:

$$F_1 = \left.\frac{\mathrm{d}U}{\mathrm{d}r}\right|_{r=r^+} = 2a\,\{(\sqrt{D \mid \Delta H \mid}) - \mid \Delta H \mid\} \tag{8}$$

(the maximum gradient of the potential function being $F_{\max} = a/2\ D$. The heat of reaction corresponding to this gradient is not excessive, $\mid \Delta H \mid = D/4$, and so in practice always that part of the curve having the maximum gradient is to be taken into account). Using (8), the transmission coefficient is given by

$$x = \frac{4\pi^2}{hva}\,\frac{e^2}{\{(\sqrt{D \mid \Delta H \mid}) - \mid \Delta H \mid\}} \tag{9}$$

and for the logarithm of the transmission coefficient

$$\log x = \text{const.} + 2 \log e - \log \{(\sqrt{D} \mid \Delta H \mid) - \mid \Delta H \mid\}. \tag{10}$$

Because of the relationship

$$\mid \Delta H \mid = D - (L_1 - L_2) \tag{11}$$

this equation leads to a dependence upon the localization energy; if the localization energy decreases (i.e. if the heat of reaction increases) the value of x slightly decreases. Experimental data, however, have shown that the log of the transmission coefficient increases linearly with decrease of the localization energy. Consequently, there must be between log e and L a considerably stronger dependence (at least in some cases) which is reversibly operative and cannot be compensated by the slight dependence discussed above.

For theroetical calculation of the transmission coefficient of non-adiabatic reactions therefore, the relationship $\log e = f(L)$ ought to be clarified. Calculation of the resonance energy of the transition state presents almost insurmountable difficulties.

As was shown, the greater the change in delocalization energy during the process the smaller will be the value of the transmission coefficient in the case of non-adiabatic reactions. In the course of the reaction, the delocalization energy may decrease (as in the case of aromatic hydrocarbons) or increase (as for quinones). With the increase of $\mid \Delta E_D \mid$ the log of the pre-exponential factor containing log x has decreased in all instances. Consequently from the point of view of the probability of the reaction, only the magnitude of the change of the delocalization energy is decisive, while its direction is of no significance. Thermodynamic considerations lead, of course, to the same conclusion.

The $x = f(\mid \Delta E_D \mid)$ relation may be expressed qualitatively by stating that the probability for the unsaturated molecule to react is the smaller, the lower its energy, i.e. the more difficult it becomes to disrupt its π-electron system.

3. THE EFFECT OF THE FORMATION OF MOLECULAR COMPOUNDS ON THE VALUE OF THE TRANSMISSION COEFFICIENT

It is thus evident that the various factors influencing reactivity exert their effects by changing the resonance energy of the transition state. In the case of charge-transfer complexes, this effect can be understood on the basis of the following qualitative considerations.

In Eqn. (2), ψ_1 and ψ_2 are strictly the wave functions of the many-electron -systems of the (inhibitor + radical) complex in the initial and final states respectively. For simplicity, we can consider ψ_1 and ψ_2 as only the total wave functions of the two electrons (which create the new bond) in the initial and final states respectively. If no complex is formed, one of the electrons has a pure π character while the wave function of the "radical" electron while basically of π character will also have slight s character. The overlap integral

$$\int \psi_1 (1, 2) \psi_2 (1, 2) \, dv_1 \, dv_2 \tag{12}$$

can be shown to be zero in spite of this slight s character. This does not necessarily imply that the integral

$$e = \int \psi_1 (1, 2) H \psi_2 (1, 2) \, dv_1 \, dv_2 \tag{13}$$

is also zero but its value is very probably small.

If a complex is formed, in which case a partial charge transfer occurs, the wave function of the complex can be described[1] by the linear combination

$$\psi_1 = a\,\phi_1 + b\,\phi_2, (a^2 + b^2 = 1) \tag{14}$$

where ϕ_1 stands for the total wave function of the donor–acceptor system without charge-transfer and ϕ_2 that for the same system in the case of transfer of one elementary charge. Since, as a result of the charge transfer, two radical-ions (a positive one and a negative one) are formed, their π-electrons will possess a slight s character also. By substituting Eqn. (14) into (2), in the case of complex formation the resonance energy of the transition state will be given by

$$e' = a \int \phi_1\, H\, \psi_2\, \mathrm{d}\tau + (\sqrt{1} - a^2) \int \phi_2\, H\, \psi_2\, \mathrm{d}\tau = a\, I_1 + (\sqrt{1} - a^2)\, I_2. \tag{15}$$

If, after the reaction, the formation of the complex ceases (i.e. if ψ_2 cannot be given in the form of a linear combination) which in the particular cases reported seems very probable, then $e' > e$ even if $I_1 = I_2$. If however $I_2 \gg I_1$, e' will be considerably larger than e.

By substituting for I_2 in (15), the wave functions of the two electrons which form the bond, the slight s character of the π-electron of the inhibitor molecule makes it possible to prove that $I_2 \gg I_1$. Increased reactivity due to the formation of complexes leads to the general conclusion that in non-adiabatic reactions all the effects which distort the π-electron symmetry of unsaturated compounds will increase the reactivity, or more exactly, the value of the transmission coefficient. In some cases, the effects of substitution are similar.

4. FURTHER CONCLUSIONS

The preceding considerations show that the formation of molecular compounds causes an increase in the reactivity of both components, at least in non-adiabatic reactions. In the case of inhibited polymerization, however, only the increase in the reactivity of the inhibitor can be observed experimentally.

The formation of molecular compounds has another interesting consequence, viz. that the "chain-regeneration reaction" (i.e. the reaction between the radical formed from the inhibitor and the monomer) has a considerable rate although otherwise it is rather rare. It seems clear that the radical formed from the inhibitor component of the molecular compound is able to react immediately with the monomer component as a consequence of the favourable steric position of the latter; this means that reaction (17) as well as (16) takes place

$$\text{—M.} + \text{ZM} \rightarrow \text{—M—Z.} + \text{M} \tag{16}$$

$$\text{—M.} + \text{ZM} \rightarrow \text{—M—Z—M.} \tag{17}$$

The observation that substituents in the inhibitor molecule with great steric requirements (so increasing the distance between the components of the molecular compound) cause a rapid decrease in the rate of the chain-regeneration process (17), is in excellent accord with the above mechanism.[6]

Finally we must mention some problems connected with copolymerization processes. Monomers with strong electron-acceptor properties (some derivatives of maleic and fumaric acids) are known to form molecular compounds with styrene. Copolymerizations involving these monomers show peculiar behaviour. The alternating tendency is here so pronounced that the different polarities of the monomers and the polymer radicals seem insufficient to explain the results properly. Also the simple treatment of copolymerization cannot be applied to these systems and it is necessary to introduce at least one further parameter, for example by considering the penultimate group effect.(15)

The possibility that in these systems molecular compounds participate has already been assumed; the idea has however been rejected.(15) Since, however, the formation of molecular compounds may increase reactivity, it is reasonable to suppose that in these systems much of the growth involves molecular compounds. By this idea, the alternating character of the copolymerization can be compared with the chain-regeneration step in the inhibited polymerization. It should be noted that in these cases the system must be treated as having at least three components and therefore up to 8 elementary reactions of chain growth. For such cases, the simple equations of copolymerization are inapplicable.

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Résumé—Les composés moléculaires (complexes de transfert de charge) qui peuvent se former au cours de certaines polymérisations radicalaires ont une grande influence sur la cinétique du processus. Nous avons étudié théoriquement les facteurs qui déterminent les paramètres des réactions entre les radicaux et leurs partenaires dans la réaction ayant lieu dans un système possédant des associations étroites par électrons-π. Nous nous sommes attachés tout spécialement à l'effet de la formation de composés moléculaires. Nous avons conclu que l'accroissement de la réactivité peut être attribué à l'accroissement de l'énergie de résonance de l'état de transition. Sur cette base, quelques effets anormaux se produisant dans des polymérisations inhibées ou des copolymérisations peuvent être interprétés de façon satisfaisante.

Sommario—I composti molecolari (complessi con trasferimento di carica) che si possono formare in alcune polimerizzazioni radicaliche influenzano notevolmente la cinetica del processo. Noi abbiamo esaminato teoricamente quei fattori che determinano i parametri delle reazioni fra radicali e i loro "partners" di reazione con un sistema di elettroni-π a guscio chiuso. Speciale attenzione é stata data all'effetto della formazione di composti molecolari. Abbiamo concluso che l'aumento della reattività può essere attribuito all'aumento dell'energia di risonanza nello stato di transizione. Su questa base, alcuni effetti anormali in polimerizzazioni inibite e in copolimerizzazioni possono avere una interpretazione soddisfacente.

Zusammenfassung—Die Molekülverbindungen (charge-transfer-Komplexe), die bei einigen Radikalpolymerisationen gebildet werden können, beeinflussen die Kinetik der Prozesse erheblich. Wir haben diejenigen Faktoren theoretisch untersucht, die die Parameter der Reaktionen zwischen Radikalen und ihren Reaktionspartnern mit einer geschlossenen π-Elektronensystem Schale bestimmen. Besondere Aufmerksamkeit wurde dabei auf den Effekt gelegt, den die Bildung molekularer Produkte hat. Wir haben gefolgert, daß die Zunahme der Reaktivität der Zunahme der Resonanzenergie des Übergangszustandes zugeschrieben werden kann. Auf dieser Basis lassen sich einige anormale Effekte in inhibierten Polymerisationen und Copolymerisationen befriedigend erklären.