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The Reactivity of Polyfunctional Compounds in Radical Reactions

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Recent results of studies of the kinetics of the reactions of monohydric and polyhydric alcohols and polyfunctional esters with peroxy- and alkyl radicals, oxygen, and hydroperoxide are examined. By comparing the reactivities of mono- and polyfunctional compounds in relation to polar reagents, it is shown that the rule of the additivity of the partial rate constants breaks down in all cases. The data are analysed within the framework of the concept of the multidipolar interaction of the polar groups in the molecule and the transition state and the complete agreement between the published results and the conclusions based on this concept is demonstrated.
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I. INTRODUCTION

The reactivity of molecules in radical reactions depends both on their structure and on the structure of the attacking radical. The following factors influence the reactivity of molecules in radical abstraction and addition reactions. The first factor is the heat of reaction: the higher the heat, the faster the reaction; the dependence of the activation energy on the heat of reaction within the limits of a single reaction series can be fitted by the Polanyi–Semenov equation.[1] The second factor is the polarity (polar structure) of the transition state: the shift of electron density in the transition state from one atom to another lowers the activation energy.[2] The third is the steric factor associated with the presence of bulky substituents adjoining the reaction centre which hinder the attack by the radical.[2] All three factors depend on the nature of the atoms participating in the reaction and on the structure of the substituents. The molecule of an organic compound can therefore be subjected to an imaginary sub-division into a series of fragments and the reaction rate constant can be represented by the sum of the partial rate constants referred to the corresponding fragments. This additivity rule for radical reactions frequently holds satisfactorily and is fairly widely used.[3]

Comparison of the rate constants for the reactions of peroxy-radicals with monocarboxylic and dicarboxylic acid esters[4] and also for the reaction of the cumenylperoxy-radicals with diethylene glycol dicaprylate and pentaerythritol tetravalerate[5] revealed the failure of this rule. These facts served as the starting point for the development of the concept of the dipole–dipole interaction between the polar agent and the dipole moments of the polar groups in the polyfunctional molecule,[6] which has been referred to as multidipolar interaction, since several (more than two) dipolar groups are involved in it. Evidence concerning the validity of the above concepts has been obtained very recently for a wide variety of radical reactions. This review is devoted to the analysis and survey of these data.

II. THE STRUCTURAL FACTORS WHICH DETERMINE THE REACTIVITY OF MOLECULES

The rate constant for the elementary reaction of a radical with a molecule depends on the heat of reaction (the Polanyi–Semenov rule), the polarity of the transition state, the accessibility of the reaction centre, and the temperature and nature of the medium. The reactivity of the molecule is influenced by bond conjugation, by the inductive effect, and by the steric factor.

Each of the three factors indicated can influence the heat of reaction. The scale of this influence can be inferred by comparing the C–H bond strengths in the corresponding compounds. For example, the contribution of the conjugation effect can be estimated by comparing the C–H bond strengths in the methane (435 kJ mol^{-1}) and toluene (355 kJ mol^{-1}) molecules.[7] The difference of 80 kJ mol^{-1} is caused in this case by the fact that the free valence in the benzyl radical is conjugated with the π orbitals of the benzene ring. The decrease of the C–H bond dissociation energy from 435 kJ mol^{-1} in methane to 410 kJ mol^{-1} in methyl bromide is associated with the polar effect exerted by the bromine atom.[7] In ethanol the energy of the α-C–H bond is lower by 34 kJ mol^{-1} than in ethane, where D_{C-H} = 410 kJ mol^{-1} [7] owing to the combined influence of the inductive effect (the shift of the σ electrons along the C–O bond) and the effect of the conjugation of the free valence with the pair of p electrons of oxygen. Comparison of ethylbenzene and indan may serve as an example of the influence of the steric effect on the C–H bond strength. The methyl group in the α-phenylethyl radical prevents the most complete overlap of the p orbital of the unpaired electron with the π orbitals of the benzene ring. The α-C–H bond in ethylbenzene is therefore somewhat stronger than in indan and the phenyl radical attacks the indan α-C–H bond four times faster than that in ethylbenzene.[8]

The polar factor, which is manifested when the radical (atom) and the molecule have different electron affinities, is also very important.[8] An example may be provided by a

comparison of the reactions of chlorine and hydrogen with methane. Since the H–H and H–Cl bond strengths are equal (426 kJ mol^{-1}), it follows that the heats of these two reactions are also equal (−8 kJ mol^{-1}). Nevertheless the activation energies for these reactions differ by 38 kJ mol^{-1}: E = 54 kJ mol^{-1} for the reaction of hydrogen with methane and E = 16 kJ mol^{-1} for the reaction of chlorine with methane.[9] Such a marked decrease of activation energy on passing from H to Cl has been accounted for by the polar structure of the transition state Cl...H...CH_3 in which the Coulombic attraction in the fragments bearing unlike charges reduces the potential barrier. The polar structure of the transition state is determined in its turn by the high electron affinity of the chlorine atom (346 kJ mol^{-1}).

The inductive effect influences both the heat of reaction and the polar character of the transition state. For example, in the reactions of bromine atoms with the C–H bonds of cyclohexane and toluene the principal factor is the heat of reaction. The C–H bond in toluene (D_{R-H} = 355 kJ mol^{-1}) is much weaker than in cyclohexane (D_{R-H} = 393 kJ mol^{-1}) [7] and toluene is accordingly brominated 17 times faster than cyclohexane (at 353 K).[8] On the other hand, chlorine atoms attack cyclohexane molecules four times faster than toluene molecules (at 313 K).[8] This "inversion" of the reactivities of the molecules can be accounted for by the different contributions of the heat of reaction and the polar factor to the activation energy for the reaction. The reaction of bromine with toluene is thermally neutral, while that with cyclohexane is endothermic (q = 38 kJ mol^{-1}) and the relative reactivities of toluene and cyclohexane are therefore determined by the strengths of their C–H bonds. while the polar structure is of secondary importance.

The reaction of chlorine (D_{H-Cl} = 426 kJ mol^{-1}) is extremely exothermic with both toluene (q = 71 kJ mol^{-1}) and cyclohexane (q = 33 kJ mol^{-1}).[7] The polar effect, which is greater in the case of cyclohexane, therefore makes a decisive contribution to the decrease of activation energy.

Another example involves the attack by various species on the C–H bonds in the propionic acid molecule.[8] The methyl radical attacks predominantly the α-CH_2 group (at 373 K the α-C–H bond is attacked 8 times faster than the β–C–H bond). On the other hand, the chlorine atom attacks the stronger β–C–H bond 33 times faster than the weaker α–C–H bond (at 353 K). The ratio of the rate constants for the methyl radical is determined by the strengths of these bonds. On the other hand, the chlorine atom attacks faster in those cases where a more polar transition state is produced; this is hindered by the presence of the electron-accepting carboxy-group in the α-position. A relation between the rate constant, on the one hand, and the ionisation potential of the molecule I(RH) and the electron affinity of the peroxy-radical EA($RO_2^{\cdot}$), on the other, has been found empirically for the reactions of peroxy-radicals with aromatic alkyl-substituted hydrocarbons;[10] at 348 K the relation is of the form $\Delta \lg k = 31.48\ [I(RH) - EA(RO_2^{\cdot})]^{-1}$.

Finally, the third factor determining the reactivity is the accessibility of the reaction centre, which depends on the size and number of the bulky substituents near the reaction centre and on the conformation of the molecule. For example, the phenyl radical abstracts an H atom from hydrocarbons having the structure $(CH_3)_3C(CH_2)_nCH(CH_3)_2$ with relative rate constants of 0.71 (n = 0), 0.34 (n = 1), and 0.81 (n = 2),[8] i.e., instead of a smooth increase of the rate constant with increasing n, its decrease (by a factor of two) on passing from n = 0 to n = 1, i.e. after the appearance of one CH_2 group, is observed. An analogous relation (a periodic relation as a function of the number of CH_2 groups) has been observed for the reactions of the undecyl radical with the esters $CH_3OCO(CH_2)_nCOOCH_3$.[11]

All three effects (the inductive effect, the conjugation effect, and the steric effect) are local in character. The inductive effect is transmitted via the σ-bonds and rapidly decays: at the third carbon atom starting from the atom attached to a polar substituent it is no longer manifested. For the manifestation of an appreciable influence of the conjugation effect, a double bond or an aromatic ring must adjoin this atom (i.e. must be located in the 2-position). The steric effect is also manifested only in the vicinity (in the α-position and more weakly in the β-position) of the bulky substituent. The molecule whose C–H bonds are attacked by free radicals can therefore be subdivided into a series of structural groups, each of which enters into the reaction with its own partial rate constant. The rule of the additivity of the partial rate constants follows from this approach: the rate constant for the reaction of a free radical with a molecule is equal to the sum of the partial rate constants k_i for all the fragments constituting the molecule, i.e.

$$k = \sum_i^n k_i.$$

The rule of additivity holds fairly well in many cases. For example, it has been clearly established that, in the reactions of free radicals with hydrocarbons,[3] aliphatic acids, and esters, the reaction rate constant increases linearly with the number of methylene groups.[4] Table 1 presents the partial rate constants for the reactions involving the abstraction of a hydrogen atom by the $CH_3^{\cdot}$, $RO^{\cdot}$, and $RO_2^{\cdot}$ radicals.

Table 1. The partial rate constants (k, litre mol^{-1} s^{-1}) for the abstraction of H atoms from the C–H bonds in various groups.

Group	$CH_3^{\cdot}$ (338 K) [3]	$(CH_3)_3OO^{\cdot}$ (313 K) [3]	$(CH_3)_3COO^{\cdot}$ (303 K) [12]
$-CH_3$	5.0	$2.5\cdot10^4$	—
$>CH_2$	50	$1.4\cdot10^5$	$2.7\cdot10^{-4}$
$\equiv CH$	500	$3.8\cdot10^5$	$4.8\cdot10^{-3}$
$>C{=}CHCH_3$	18	$4.8\cdot10^5$	—
$>C{=}CHCH_2{-}R$	120	$1.4\cdot10^4$	$8.4\cdot10^{-2}$
$C_6H_5{-}CH_3$	420	$2.4\cdot10^5$	$1.2\cdot10^{-2}$
$C_6H_5{-}CH_2R$	560	$1.6\cdot10^5$	0.10
$C_6H_5CH(CH_3)_2$	$1.8\cdot10^3$	$8.4\cdot10^4$	0.16
$>CHOH$	$3.4\cdot10^3$	—	$9\cdot10^{-3}$
$-CO-CH_2-$	850	$8.5\cdot10^4$	—

Note. The numerals in square brackets denote references (Ed. of Translation).

The rule of additivity is well known from experiments involving the reactions of atoms (H, Cl, Br) and free radicals ($HO^{\cdot}$, $RO_2^{\cdot}$, $CH_3^{\cdot}$, $CF_3^{\cdot}$) with hydrocarbons and monofunctional organic compounds.[3] The rule also holds for reactions of peroxy-radicals with hydrocarbons. Even in the oxidation of dicarboxylic acids and their esters, it holds in relation to the methylene groups in the molecule.[4] For example, the rate constants for the reaction of cumenylperoxy-radicals with the dimethyl esters of dicarboxylic acids increase linearly with increase in the number n of methylene groups in the acid residue: $\log k = 9.6 + 0.73n$ litre $mole^{-1}$ s^{-1} at

413 K. The situation is exactly the same for the dependence of k on the number of CH_2 groups in the alcoholic residue when the cumenylperoxy-radical attacks the molecule of a dibasic acid ester and the alcohol residue in the molecule is varied.[4] However, as shown below, in many reaction series the rule of the additivity of the partial rate constants does not hold, i.e. for a molecule consisting of n fragments we have

$$k \neq \sum_i^n k_i,$$

where k_i refers to the ith fragment. The deviation from the additivity rule can be characterised, for example, by the ratio

$$\sum k_i/k$$

or its logarithm. Using the theory of the absolute reaction rates, the deviation can be characterised in terms of the change in the Gibbs free energy of activation as

$$\Delta\Delta G_{ad}^{\neq} = \Delta G^{\neq} - \Delta G_{ad}^{\neq} = RT \ln \left(\sum_i k_i/k \right),$$

where $\Delta G_{ad}^{\neq}$ is the Gibbs activation energy for the molecule when the rule of additivity holds.

III. THE REACTIONS OF PEROXY-RADICALS WITH POLYHYDRIC ALCOHOLS AND POLYFUNCTIONAL ESTERS

Valuable experimental data on the reactivities of polyfunctional esters in reactions with cumenylperoxy-radicals have been obtained in the study of the oxidation of the esters in the presence of cumenyl hydroperoxide, which serves simultaneously also as the initiator of the reaction and as the source of cumenylperoxy-radicals.[11,13] The experimental conditions ensured in the system an intense exchange of the $RO_2^{\cdot}$ radicals for cumenylperoxy-radicals. The chain oxidation scheme in a system of this kind includes the following reactions:

$$\mathrm{ROOR} \xrightarrow{k_i} 2\mathrm{RO}^{\cdot} \xrightarrow{\mathrm{R'H}} \dot{\mathrm{R}}';$$

$$\mathrm{ROOH} \xrightarrow{k_{i,\mathrm{ROOH}}} \mathrm{RO}^{\cdot} + {}^{\cdot}\mathrm{OH} \xrightarrow{\mathrm{R'H}} \dot{\mathrm{R}}';$$

$$\dot{\mathrm{R}}' + \mathrm{O}_2 \rightarrow \mathrm{R'OO}^{\cdot};$$

$$\mathrm{R'OO}^{\cdot} + \mathrm{ROOH} \rightleftharpoons \mathrm{R'OOH} + \mathrm{RO}_2^{\cdot};$$

$$\mathrm{R'OO}^{\cdot} + \mathrm{R'H} \xrightarrow{k_p'} \mathrm{R'OOH} + \dot{\mathrm{R}}';$$

$$\mathrm{RO}_2^{\cdot} + \mathrm{R'H} \xrightarrow{k_p} \mathrm{ROOH} + \dot{\mathrm{R}}';$$

$$\mathrm{RO}_2^{\cdot} + \mathrm{RO}_2^{\cdot} \xrightarrow{k_t} \mathrm{ROOR} + \mathrm{O}_2;$$

$$\mathrm{R'O}_2^{\cdot} + \mathrm{RO}_2^{\cdot} \xrightarrow{k_t'} \mathrm{R''{=}O} + \mathrm{O}_2 + \mathrm{ROH};$$

$$\mathrm{R'O}_2^{\cdot} + \mathrm{R'O}_2^{\cdot} \xrightarrow{k_t''} \mathrm{R''{=}O} + \mathrm{O}_2 + \mathrm{R'OH}.$$

For sufficiently long chains and when the reaction of $\dot{R}'$ with O_2 is very rapid, the rate of chain oxidation is described by the expression $v_{\vee} = \{k_p[RO_2^{\cdot}] + k_p'[R'O_2^{\cdot}]\}[RH] = a[RH]v_i^{1/2}$; the variation of the ratio $[ROOH]/[R'H]$ entails the variation of the coefficient a, which depends on the composition of the radicals, i.e. on the ratio $[RO_2^{\cdot}]/[R'O_2^{\cdot}]$. When $[ROOH] = 0$, the coefficient $a = k_p'(2k_t'')^{-1/2}$, and when $[ROOH] \to \infty$, we obtain $a \to k_p(2k_t)^{-1/2}$. The experiments were performed for $[ROOH] \geqslant 0.8$ M,[13] whereupon the coefficient a reaches its maximum value of 6×10^{-3} litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$. The results of the measurement of $k_p(2k_t)^{-1/2}$ are presented in Table 2. The absolute values of k_p were calculated on the assumption that $2k_t = 4.05 \times 10^6$ litre mol^{-1} s^{-1} for cumenyl peroxide.[15]

With increase of the number of ester groups in the molecule, the partial rate constant k_{pi} also increases. If it is assumed, after Pozdeeva et al.,[14] that $\Delta \lg k_{pt} = \delta n$, where n is the number of ester groups, then we obtain $k_{pi} = 1.0$ litre mol^{-1} s^{-1} for the monoester ($n = 1$). This makes it possible to calculate $\Delta\Delta G_{ad}^{\neq}$, which varies in the series of propionate esters from 0 to −4 kJ mol^{-1}. In this series of compounds, the increase of the number of functional groups in the molecule increases the reactivity of the C−H bonds in each group. Another tendency has been observed for esters obtained from different aliphatic acids. Only the $-OCH_2-$ groups are apparently attacked in pentaerythritol tetraacetate, so that $k_{CH_2O} = 0.25\, k_p = 2.0$ litre mol^{-1} s^{-1}. For the attack by the cumenylperoxyradical on the α-CH_2 group of the acid residue in pentaerythritol tetrapropionate, we obtain $k_{\alpha\text{-}CH_2} = 0.25k_p - 2.0 = 1.5$ litre mol^{-1} s^{-1}. For pentaerythritol tetracaprate, the average value of k_{CH_2} for the methylene groups in the acid residue is significantly higher: $k_{CH_2} = (87.7 - 8.1)/32 = 2.5$ litre mol^{-1} s^{-1}. In the n-heptadecane molecule (see Table 3 below) the methylene group reacts with $RO_2^{\cdot}$, for which $k_{CH_2} = 2.8$ litre mol^{-1} s^{-1}.

Table 2. Kinetic parameters of the oxidation reaction of esters in the presence of cumenyl hydroperoxide (404 K, *o*-dichlorobenzene).[13,14]

Ester	$k_p'(2k_t'')^{-1/2} \times 10^3$, litre$^{1/2}mol^{-1/2}s^{-1/2}$	k_p, litre mol^{-1}s^{-1}	k_p^0, litre mol^{-1}s^{-1}*	$\Delta\Delta G_{ad}^{\neq}$, kJ mol^{-1}
$C(CH_2OCOCH_3)_4$	2.82	8.1	2.0	—
$C(CH_2OCOCH_2CH_3)_4$	3.69	13.9	3.5	−4.1
$CH_3CH_2C(CH_2OCOCH_2CH_3)_3$	2.62	6.4	2.1	−2.5
$(CH_3)C(CH_2OCOCH_2CH_3)_2$	1.27	3.0	1.5	−1.4
$CH_3CH_2OCO(CH_2)_3CH_3$	2.26	5.0	5.0	—
$C[CH_2OCO(CH_2)_6CH_3]_4$	26.2	87.7	22	—
$[CH_2OCO(CH_2)_6CH_3]_2$	8.65	28.5	—	—
$[CH_2OCH_2CH_2OCO(CH_2)_6CH_3]_2$	15.84	54.7	—	—
n-$C_{17}H_{36}$	12.50	41.7	2.8	—

*Here k_p^0 represents the constant recalculated for one fragment.

Evidently the ester group lowers the reactivity of the nearest methylene groups of the acid residue and, on moving away from the OCO group, the reactivity of the methylene groups increases, tending to that in an n-paraffin molecule.

The coupled oxidation of a number of ethers and esters with n-decane has been studied.[16] The ratio of the rate constants for the reactions of decylperoxy-radical with the ester or ether and n-decane has been estimated from the dependence of the rate of the initiated oxidation on the concentration of the ester or ether added to the hydrocarbon. The relative partial rate constants (at 403 K) were obtained from a comparison of the relative rates with the structures of the monofunctional esters and ethers: 0.125 for the CH_2 group, 2.4 for the OCH_2 group, and 0.4 for the CH_2OCO. $.(CH_2)_6$ group. Calculation assuming additivity for diethylene glycol dicaprylate yielded $k_{rel} = 5.2$, while the experimental value is 2.8. $\Delta\Delta G_{ad}^{\neq} = 2.1$ kJ mol^{-1} corresponds to this deviation from additivity.

Apart from ethers and esters, the reactivity of polyhydric alcohols in reactions with peroxy-radicals has been investigated.[16,17] This reaction has been studied[17] by the method of coupled oxidation with a selective inhibitor,[18] in which the ability of peroxy-radicals derived from the alcohol to reduce certain compounds, particularly quinones, was used.[19] Under the conditions of the coupled chain oxidation, such a selective inhibitor lowers the rate of the process to an extent which depends on the rate of generation of the hydroxyperoxy-radicals from the alcohol: the faster the formation of these radicals, the more pronounced the inhibiting effect of the inhibitor. This makes it possible to determine the reactivity of the alcohol in relation to $RO_2^{\cdot}$ compared with the reactivity of RH. In the presence of a selective inhibitor Q (quinone) and an initiator I, the coupled oxidation of an alcohol HR'OH and the substance RH includes the following stages:[18]

$$I \xrightarrow{v_i} \dot{r} \xrightarrow{RH} \dot{R} \xrightarrow{O_2} RO_2^{\cdot};$$

$$RO_2^{\cdot} + RH \xrightarrow{k_p} ROOH + \dot{R};$$

$$RO_2^{\cdot} + HR'OH \xrightarrow{k_p'} ROOH + \dot{R}'OH;$$

$$O_2 + \dot{R}'OH \xrightarrow{fast} \dot{O}OR'OH;$$

$$\dot{O}OR'OH + Q \rightarrow \dot{Q}H + O_2 + R'{=}O;$$

$$RO_2^{\cdot} + \dot{Q}H \xrightarrow{fast} ROOH + Q;$$

$$RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_t} \text{products}.$$

At a sufficiently high concentration of Q in the system, the $RO_2^{\cdot} + RO_2^{\cdot}$ reaction does not play any role in chain termination and the peroxy-radicals derived from the alcohol react with Q so fast that the rate of reaction is limited by their formation via the reaction of $RO_2^{\cdot}$ with the alcohol.

Under these conditions, the rate of the inhibited oxidation is defined by the expression

$$v = k_p[RH][RO_2^{\cdot}] + v_i \cong k_p[RH][RO_2^{\cdot}],$$

where

$$v_i = 2k_p'[HR'OH][RO_2^{\cdot}],$$

and the rate constant ratio k_p'/k_p is found from the equation $k_p'/k_p = v_i[RH]/2v[HR'OH]$. Degtyareva et al.[16] carried out experiments under conditions such that the chains are short (the chain length was $\nu < 10$) and the degree of inhibition was low ($v/v_0 > 0.3$). Under these conditions, it is not permissible to neglect either v_i or the contribution by the $RO_2^{\cdot} + RO_2^{\cdot}$ reaction, i.e. it is necessary to take into account the fact that the following equalities hold in the quasi-stationary regime in the presence of Q: $k_p[RH][RO_2^{\cdot}] = v - v_i$ and $v_i = 2k_p'[HR'OH][RO_2^{\cdot}] + 2k_t[RO_2^{\cdot}]^2$. Bearing in mind that $v = v_0 = k_p(2k_t)^{-1/2}[RH]v_i^{1/2}$ when [Q] = 0, we arrive at the following formula after simple rearrangements:

$$\frac{k_p'}{k_p} = \frac{1}{2}\frac{[RH]}{[HR'OH]}\left\{\frac{1}{\nu - 1} - \frac{\nu - 1}{\nu_0^2}\right\},$$

where $\nu = v/v_i$ and $\nu_0 = v_0/v_i$. This formula is more accurate than that quoted in Ref.17 and was used to recalculate the k_p'/k_p ratios from the experimental data of the earlier study.[17] The results of the calculation are presented in Table 3.

$\Delta\Delta G_{ad}^{\neq}$ can be estimated more conveniently for the absolute values of k_p'. Following the procedure of Degtyareva et al.,[16] we assume that k_p is the same as for the reaction of cumenylperoxy-radicals with n-hexadecane. According to Denisov et al.,[4] $k_{pi} = 0.31$ litre mol^{-1} s^{-1} at 403 K for the reaction of the cumenylperoxy-radical with one methylene group of an n-paraffin, so that we obtain $k_p = 14 \times 0.31 = 4.3$ litre mol^{-1} s^{-1} for the reaction of $RO_2^{\cdot}$ with n-hexadecane (neglecting the attack by the peroxy-radicals on the methyl groups). On the basis of data for the coupled oxidation of n-hexadecane together with 1-decanol and 2-octanol[17] and assuming that the methylene groups in the alcohol molecules are attacked with the same partial rate constant as in the n-paraffin molecule, we obtain the following partial rate constants: $k_{CH_2OH} = 34.8 - 8 \times 0.31 = 32.3$ litre mol^{-1} s^{-1} and $k_{CHOH} = 43.4 - 5 \times 0.31 = 41.9$ litre mol^{-1} s^{-1}. Proceeding in exactly the same way as for the diethylene glycol dicaprylate–alcohol system and assuming that $k_p = 4.6$ litre mol^{-1} s^{-1},[5] we obtain $k_{CH_2OH} = 22.5 - 2.5 = 20$ litre mol^{-1} s^{-1} for 1-decanol and $k_{CH_2OH} = 23.0 - 2.2 = 20.8$ litre mol^{-1} s^{-1} for 1-nonanol; these values are very close and one can adopt the average $k_{CH_2OH} = 20.4$ litre mol^{-1} s^{-1}. On the basis of the data for 2-octanol (Table 3), we obtain $k_{CHOH} = 22.5 - 1.5 = 21$ litre mol^{-1} s^{-1}. Table 4 presents the values of k_p', the constants k_Σ obtained assuming additivity, and the values of $\Delta\Delta G_{ad}^{\neq}$ calculated on this basis. It is seen that polyhydric alcohols do not obey the rule of additivity in reactions with peroxy-radicals.

Table 3. The results of the measurement of k_p'/k_p for a number of alcohols by the method of coupled oxidation in the presence of a selective inhibitor {404 K, [Q] = 10^{-2} M, initiator—di-t-butyl peroxide}.[17]

Alcohol	k_p'/k_p	
	1	2
$CH_3(CH_2)_8CH_2OH$	8.1±0.6	4.9±0.8
$CH_3(CH_2)_7CH_2OH$	—	5.0±0.4
$CH_3CHOH(CH_2)_5CH_3$	10.1±1.4	4 9±0.7
$HOCH_2CH_2OH$	3.5±0.6	—
$HOCH_2CH_2CH_2CH_2OH$	3.9±0.2	3.1±0.1
$HOCH_2CH_2CHOHCH_3$	5.2±0.2	3.4±0.3
$HOCH_2C(CH_3)_2CH_2OH$	154±37	26.3±2.1
$CH_3CH_2C(CH_2OH)_3$	42±6	25.7±4.8
$[HOCH_2CH(OH)CH_2]_2O$	70±9	15.4±0.6
$CH_3CHOHCHOHCH_3$	—	5.8±1.2

Notation: 1) results obtained in experiments with hexadecane ($v_i = 1.3 \times 10^{-6}$, $v_0 = 7.6 \times 10^{-6}$ mol litre^{-1} s^{-1}); 2) results obtained in experiments with diethylene glycol dicaprylate ($v_i = 8.3 \times 10^{-7}$, $v_0 = 8.0 \times 10^{-6}$ mol litre^{-1} s^{-1}).

The coupled oxidation of a number of monohydric and polyhydric alcohols together with n-decane, n-hexadecane, and polyfunctional esters has been investigated.[16] Experimental measurements were made of the dependence of the rate of the initiated chain oxidation on the composition of the binary mixture (at 403 K using di-t-butyl peroxide as the initiator). The following scheme comprising reactions limiting the rate of chain propagation and termination is valid for the initiated chain oxidation (RH is a hydrocarbon or ester and HR'OH is an alcohol):

$$RO_2^{\cdot} + RH \xrightarrow{k_{p,11}} ROOH + R^{\cdot};$$

$$RO_2^{\cdot} + HR'OH \xrightarrow{k_{p,21}} ROOH + \dot{R}'OH;$$

$$HOR'O_2^{\cdot} + RH \xrightarrow{k_{p,12}} HOR'OOH + R^{\cdot};$$

$$HOR'O_2^{\cdot} + HR'OH \xrightarrow{k_{p,22}} HOR'OOH + \dot{R}'OH;$$

$$\left.\begin{aligned} RO_2^{\cdot} + RO_2^{\cdot} &\xrightarrow{k_{t,11}} \\ RO_2^{\cdot} + HOR'OO^{\cdot} &\xrightarrow{k_{t,12}} \\ HOR'O_2^{\cdot} + HOR'OO^{\cdot} &\xrightarrow{k_{t,22}} \end{aligned}\right\} \text{molecular products.}$$

The rate of the coupled chain oxidation with v_i = const is described by the expression

$$v = \frac{(k_{p,11} + k_{p,12}u)\cdot[RH] + (k_{p,21} + k_{p,22}u)\cdot[HR'OH]}{(2k_{t,11} + 2k_{t,12}u + 2k_{t,22}u^2)^{1/2}} \cdot v_i^{1/2},$$

where

$$u = k_{p,21}[HR'OH]/k_{p,12}[RH].$$

For low amounts of added alcohols, where the contribution of the $HOR'OO^{\cdot}$ + HR'OH reaction to chain propagation and the contribution of the $HOR'OO^{\cdot}$ + $HOR'OO^{\cdot}$ reaction to chain termination may be neglected, the expression for the rate of the coupled oxidation assumes a simpler form:

$$\frac{v}{v_0} = \left(1 + 2\frac{k_{p,21}[HR'OH]}{k_{p,11}[RH]}\right)\cdot\left(1 + \frac{k_{t,12}}{k_{t,11}}\cdot\frac{k_{p,21}}{k_{p,12}}\cdot\frac{[HR'OH]}{[RH]}\right)^{-1/2},$$

whence the following relation can be obtained:

$$\alpha = \frac{\Delta v}{v_0}\Big/\Delta\left(\frac{[HR'OH]}{[RH]}\right) = 2\frac{k_{p,21}}{k_{p,11}} - \frac{1}{2}\frac{k_{t,12}}{k_{t,11}}\cdot\frac{k_{p,21}}{k_{p,12}},$$

where $\Delta v = v - v_0$ and $v_0 = k_p(2k_{t,11})^{-1/2}[RH]v_i^{1/2}$ is the rate of oxidation of RH in the absence of HR'OH under the same conditions. The coefficient α is determined from the experimental dependence of v on [HR'OH]/[RH].

Table 4. Deviation from additivity in the reactions of peroxy-radicals with polyhydric alcohols (403 K)*.

Alcohol (group)	k'_p/k_p	k'_p, litre mol^{-1}s^{-1}	k_Σ, litre mol^{-1}s^{-1}	$\Delta\Delta G^{\neq}_{ad}$, kJ mol^{-1}
n-Hexadecane, k_p = 4.3 litre mol^{-1}s^{-1}				
—CH_2OH	—	32.3	—	—
>CHOH	—	41.9	—	—
$HOCH_2CH_2OH$	3.5	15	64.6	4.9
$(CH_2CH_2OH)_2$	3.9	16.8	65.2	4.9
$HOCH_2CH_2CH(OH)CH_3$	5.2	22.4	74.5	4.0
$(CH_3)_2C(CH_2OH)_2$	154	662	64.6	—7.8
$CH_3CH_2C(CH_2OH)_3$	42	181	97.2	—2.1
Diethylene glycol dicaprylate, k_p = 4.6 litre mol^{-1}s^{-1}				
—CH_2OH	—	20.4	—	—
>CHOH	—	21.0	—	—
—OCH_2—	—	90	—	—
$(CH_2CH_2OH)_2$	3.1	14.3	41.4	3.6
$HOCH_2CH_2CH(OH)CH_3$	3.4	15.6	41.7	3.3
$CH_3CH(OH)CH(OH)CH_3$	5.8	26.7	42.0	1.5
$(HOCH_2)_2C(CH_3)_2$	26.3	121	40.8	—3.7
$CH_3CH_2C(CH_2OH)_3$	25.7	118	61.5	—2.2

*The ratios k'_p/k_p were taken from Table 3.

The rate constant ratio $k_{p,21}/k_{p,11}$ in which we are interested can be obtained from α by estimating the second term in the above formula, which can be done in the following manner. It is known that the reactivity of the peroxy-radical depends only slightly on its structure and one can put $k_{p,12} = k_{p,11}$. In this case the expression for the parameter α becomes

$$\alpha = 2(k_{p,21}/k_{p,11})\cdot(1 - 0.25\ k_{t,12}/k_{t,11}).$$

The ratio $k_{t,12}/k_{t,11}$ may be estimated by comparing the values of α and $k_{p,21}/k_{p,11}$ measured by the method of coupled oxidation with the selective inhibitor described above. Table 5 presents such a comparison; it is seen that always the ratio $k_{t,12}/k_{t,11} > 1$ and the average value is 2.5 ± 0.6. We obtain the formula

$$k_{p,21}/k_{p,11} = 1.33\alpha.$$

for the calculation of $k_{p,21}/k_{p,11}$. We recalculated the values of $k_{p,21}/k_{p,11}$ from the data of Degtyareva et al.[16] in terms of this formula and the results are presented in Table 6.

In order to calculate the partial rate constants, we proceed in the following way. For the alcohol–hexadecane system, where all the methylene groups in RH are equivalent as regards their reactivity, we have $k_{p,11} = 14k_{CH_2}$ and $k_{p,21}/k_{p,11} = 14k_{p,21}/k_{CH_2}$. In the n-decane molecule the peroxy-radical attacks 8 methylene groups and the CH_2OH group; consequently

$$k_{p,21}/k_{CH_2} = 74.2 = k_{CH_2OH}/k_{CH_2} + 8,$$

whence

$$k_{CH_2OH}/k_{CH_2} = 66.2.$$

Analogously, on the basis of the ratio $k_{p,21}/k_{CH_2}$ for 2-octanol, we obtain $k_{CHOH}/k_{CH_2} = 156$. Using the rule of additivity, we obtain $k_{p,21}/k_{CH_2}$ for butane-1,3-diol and for 1,1,1-tri(hydroxymethyl)propane (Table 6).

Table 5. Comparison of the values of α and $k_{p,21}/k_{p,11}$ for coupled chain oxidation of alcohols together with n-hexadecane (403 K).

Alcohol	α [13]	$k_{p,21}/k_{p,11}$ [16]	$k_{t,12}/k_{t,11}$
$CH_3(CH_2)_8CH_2OH$	4.0	8.1	3.0
$CH_3CH(OH)(CH_2)_5CH_3$	8.4	10.1	1.7
$CH_3CH_2C(CH_2OH)_3$	18	42	3.1
$CH_2CH(OH)CH_2CH_2OH$	5.4	5.2	2.1

Note. The numbers in square brackets denote references (Ed. of Translation).

Table 6. The results of the study of the coupled oxidation of alcohols together with n-hexadecane and esters (403 K, initiator—di-t-butyl peroxide).[16]

RH	HR'OH(R'H)	α	$k_{p,21}/k_{p,11}$	$k_{p,21}/k_{CH_2}$	$k_{p,21}/k_{CH_2}$ (calc.)	$\Delta\Delta G^{\neq}_{ad}$, kJ mol^{-1}
$CH_3(CH_2)_{14}CH_3$	$CH_3(CH_2)_8CH_2OH$	4.0	5.3	74.2	742	—
»	$CH_3CH(OH)(CH_2)_5CH_3$	8.4	11.2	161	161	—
»	$HOCH_2CH_2CH(OH)CH_3$	5.4	7.2	101	223	2.6
»	$CH_3CH_2C(CH_2OH)_3$	17.7	23.5	329	119.6	—1.7
$[CH_2OCH_2CH_2OCO(CH_2)_6CH_3]_2$	$CH_3(CH_2)_8CH_3$	0.17	0.2	0.025	0.025	—
»	$CH_3(CH_2)_8CH_2OH$	1.6	2.1	84	84	—
»	$CH_3CH_2(CH_2OH)_3$	7.8	10.4	416	229	—2.0
$C[CH_2OCO(CH_2)_3CH_3]_4$	$CH_3(CH_2)_8CH_3$	0.8	1.1	0.14	0.14	—
»	$CH_3(CH_2)_8CH_2OH$	2.4	3.2	22.9	22.9	—
»	$HOCH_2CH_2CH(OH)CH_3$	2.4	3.2	22.9	50.4	2.6
»	$HOCH_2CH_2CH_2CH_2OH$	2.0	2.7	19.3	30.4	1.5
»	$CH_3CH(OH)CH(OH)CH_3$	2.2	2.9	20.7	70.4	4.1

In the alcohol (hydrocarbon)–diethylene glycol dicaprylate binary system it is possible to employ as the reference value the ratio $k_{p,21}/k_{p,11}$ for n-decane, for which $k_{p,21} = 8k_{CH_2}$ and $k_{p,21}/k_{p,11} = 0.2$, whence $k_{CH_2}/k_{p,11} = 0.025$. The

partial rate constant k_{CH_2OH} can be found from the ratio $k_{p,21}/k_{p,11}$ for *n*-decanol; $k_{CH_2OH}/k_{CH_2} = 84 - 8 = 76$.

Proceeding analogously for the alcohol (hydrocarbon)–pentaerythritol tetravalerate system, we find

$$k_{p,21}/k_{CH_2}=7.86 \quad (k_{p,21}/k_{p,11})$$

and for the CH_2OH group we have $k_{CH_2OH}/k_{CH_2} = 22.9 - 8 = 14.9$. The ratio k_{CHOH}/k_{CH_2} for the secondary alcohol group can be estimated assuming that the ratio k_{CHOH}/k_{CH_2OH} is the same as for the hexadecane peroxy-radicals, where it is 2.36; we obtain $k_{CHOH}/k_{CH_2} = 2.36 \times 14.9 = 35.2$. Evidently, the ratios k_{CH_2OH}/k_{CH_2} for hexadecane and diethylene glycol dicaprylate are similar (66 and 76), while that for pentaerythritol tetravalerate is significantly lower (15). Since the oxidation of the latter ester results in the preferential formation of peroxy-groups with a quaternary carbon atom in the α-position, the steric effect is apparently the cause of the reduced reactivity of the peroxy-radicals formed from this ester.

Comparison of the calculated ratios $k_{p,21}/k_{CH_2}$ with the value obtained assuming the additivity of the partial rate constants shows that the additivity rule does not hold for polyhydric alcohols; the values of $\Delta\Delta G^{\neq}_{ad}$ vary from −2 to +4 kJ mol^{-1}. Comparison of the estimates obtained by different methods on the whole indicates a satisfactory agreement: in hecadecane $\Delta\Delta G^{\neq}_{ad} > 0$ for the reaction of $RO_2^{\cdot}$ with butane-1,3-diol and $\Delta\Delta G^{\neq}_{ad} = -2.1$ kJ mol^{-1} (Table 4) and −1.7 kJ mol^{-1} (Table 6) for the reaction of $RO_2^{\cdot}$ with 1,1,1-tri(hydroxymethyl)propane. In diethylene glycol dicaprylate the sign and magnitude of $\Delta\Delta G^{\neq}_{ad}$ for the reaction of $RO_2^{\cdot}$ with 1,1,1-tri(hydroxymethyl)propane agree fairly well [−2.0 kJ mol^{-1} (Table 4) and −2.2 kJ mol^{-1} (Table 6)]. The tendency defined by the inequality $\Delta\Delta G^{\neq}_{ad} > 0$ is maintained for the reactions of $RO_2^{\cdot}$ with alcohols in which the hydroxy-groups are located at different carbon atoms of the carbon skeleton and $\Delta\Delta G^{\neq}_{ad} < 0$ for alcohols with the $-C(CH_2OH)_n$ group ($n = 3$).

In the oxidation of unsaturated compounds peroxy-radicals abstract hydrogen atoms from the olefin molecule and add to the double bond. In the oxidation of monomers such as acrylic acid, methacrylic acid, and their esters peroxy-radicals add preferentially to the double bond with formation of polyperoxides.[20] The addition of cumenylperoxy-radicals to the double bonds of a number of unsaturated monoesters and polyesters has been investigated.[21] Each ester (Table 7) was oxidised in the presence of cumenyl hydroperoxide, which was introduced in an amount ensuring the complete replacement of the ester peroxy-radicals by the cumenylperoxy-radicals. The oxidation was carried out at 323 K with azobisisobutyronitrile as the reaction initiator (the initiation rate constant was 2.2×10^{-6} s^{-1}). The process was carried out in a chain regime and the rate of oxidation was measured manometrically, corrections being applied for the evolution of N_2 on decomposition of the initiator and the evolution of O_2 on recombination of the cumenylperoxy-radicals. The reaction scheme (M = monomer) has the following form:

$$\begin{gathered}
I \rightarrow \dot{r} \xrightarrow{O_2} rO_2^{\cdot} \xrightarrow{ROOH} RO_2^{\cdot} \xrightarrow{M} \dot{M}\ ; \\
M^{\cdot} + O_2 \rightarrow MO_2^{\cdot}\ ; \\
MO_2^{\cdot} + HOOR \rightarrow MOOH + RO_2^{\cdot}\ ; \\
RO_2^{\cdot} + M \xrightarrow{k_p} \dot{M}\ ; \\
RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_t} ROOR + O_2\ ; \\
RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_t'} 2RO^{\cdot} + O_2\ ; \\
RO^{\cdot} + HOOR \rightarrow ROH + RO_2^{\cdot}\ .
\end{gathered} \qquad (i)$$

The rate constants k_p, calculated from the experimental data assuming that the probability of the liberation of radicals into the bulk is 0.5 (Denisov[3]) and with the ratio $k_t'/k_t = 6.3$ (Howard[22]), are listed in Table 7. Comparison of the constants k_p and k_Σ (the latter were calculated assuming additivity) shows that the rule of additivity breaks down also in this group of reactions and to a greater extent the greater the number of ester groups in the molecule.

Table 7. The rate constants for the reaction of cumenyl-peroxy-radicals with the double bonds unsaturated esters (323 K).[21]

Ester	k_p, litre mol^{-1}s^{-1}	k_p/n litre mol^{-1}s^{-1}*	$\Delta\Delta G^{\neq}_{ad}$, kJ mol^{-1}
$CH_3CH{=}CHCOOCH_3$	0.50	0.50	—
$(CH_3)_2C(OCOCH{=}CHCH_3)_2$	0.76	0.38	0.8
$CH_3CH_2C(CH_2OCOCH{=}CHCH_3)_3$	1.05	0.35	1.0
$C(CH_2OCOCH{=}CHCH_3)_4$	1.28	0.32	1.2
$CH_3CH{=}C(CH_3)COOCH_3$	1.79	1.79	—
$CH_3CH_2C[CH_2OCOCCH_3{=}CHCH_3]_3$	3.93	1.31	0.9
$C[CH_2OCOC(CH_3){=}CHCH_3]_4$	3.08	0.77	2.3

*The reaction rate constant calculated for one double bond.

IV. THE REACTIONS OF POLYFUNCTIONAL ESTERS WITH HYDROPEROXIDE AND OXYGEN

In the oxidation of organic compounds in the absence of initiators (including hydroperoxide), free radicals are generated via reactions involving molecular oxygen. Three chain initiation and oxidation reactions are known to have been investigated.[23] In the first, O_2 attacks the weakest C–H bond in the molecule with formation of alkyl and hydroperoxy-radicals:

$$RH + O_2 \rightarrow \dot{R} + HO_2^{\cdot}\ .$$

The reaction is endothermic and its heat is $q = -D_{R-H} + 221$ kJ mol^{-1}. In the second, compounds with weak C–H bonds, whose dissociation energy is less than 340 kJ mol^{-1}, enter into a faster termolecular reaction with oxygen:

$$RH + O_2 + HR \rightarrow \dot{R} + H_2O_2 + \dot{R}\ ,$$

whose heat is $q = -2D_{R-H} + 570$ kJ mol^{-1}. In the third, unsaturated compounds combine with oxygen at the double bond to form a biradical:

$$XHC{=}CH_2 + O_2 \rightarrow X\dot{C}HCH_2OO^{\cdot}\ .$$

In the reaction of RH with O_2 the initial species (oxygen, is non-polar, but the R...H...O_2 group, having a non-zero dipole moment, is formed in the transition state. The configuration of the transition state is close to that of the final products ($\dot{R}$ and $HO_2^{\cdot}$) and the dipole moment of $HO_2^{\cdot}$ is 2 D (according to Opeida's estimate[10]). In the reaction of O_2 with a double bond in the transition state a non-polar O_2 molecule is converted into a polar peroxy-radical. It is entirely possible that the formation of the radical is preceded by the formation of an intermediate of the type of the charge-transfer complex $\bar{O}_2...\overset{+}{C}H_2{-}\dot{C}HX$, which has a large dipole moment. In this case too the effect of the multidipolar interaction should be observed.

Studies have been made[24,25] of chain initiation in the oxidation of ethyl propionate (by the mixed initiation method) and diethyl sebacate (by the inhibitor method using the *NN*-di-β-naphthyl-*p*-phenylenediamine inhibitor). In both cases radicals are formed via the bimolecular reaction of oxygen with the ester C–H bonds:

$$v_{i0}=k_{i0}[RH][O_2].$$

The weakest C–H bonds are the α-C–H bonds in the alcohol residue, which in fact make a decisive contribution to initiation. This has been demonstrated by studying the chain initiation in diethyl sebacate deuteriated at the α-C–H bonds of the alcohol residue: deuteriated diethyl sebacate reacts with O_2 much more slowly, as can be seen from a comparison of the values of v_{i0}:[25]

	$10^8 v_{i0}$ (413 K)	$10^8 v_{i0}$ (433 K)
Diethyl sebacate	1.4	5.4
Diethyl [α-D_2] sebacate	0.26	0.7
Kinetic isotope effect	5.2	7.4

Table 8 presents the results of the study of the chain initiation in the aliphatic esters of a number of polyhydric alcohols. It is seen that k_{i0} for pentaerythritol tetrapropionate is approximately twice as high as for the tetraacetate. Consequently the C–H bonds in both the alcohol and acid residues participate in chain initiation. When calculated per ester fragment, the constant k_{i0} varies from ester to ester, i.e. additivity breaks down for this reaction also. A very large difference is observed between the constants k_{i0} for ethyl propionate and diethyl sebacate. An approximately tenfold difference between the k_i is also observed for the addition of oxygen to the double bond in acrylic esters ($\Delta\Delta G^{\neq}_{ad}$ = 7 kJ mol^{-1}).

Table 8. The rate constants for the reactions of oxygen with saturated and unsaturated esters.[24–26]

Ester*	T, K	k/n, litre mol^{-1}s^{-1}	$\Delta\Delta G^{\neq}_{ad}$, kJ mol^{-1}	E, kJ mol^{-1}	A, litre mol^{-1}s^{-1}
$(CH_3)_3CR_2$	423	$6\cdot10^{-7}$	—	—	—
$C_2H_5CR_3$	423	$4\cdot10^{-7}$	—	—	—
CR_4	423	$1.2\cdot10^{-6}$	—	—	—
$C(CH_2OCOCH_3)_4$	423	$6\cdot10^{-7}$	—	—	—
$C_2H_5OCOC_2H_5$	433	$4.7\cdot10^{-3}$	—	133.8	$6.5\cdot10^{13}$
$(C_2H_5)_2[OCO(CH_2)_4]_2$	433	$4.2\cdot10^{-6}$	25.3	141.7	$5.2\cdot10^{11}$
$H_2C{=}CHCOOC_4H_9$	473	$7.6\cdot10^{-7}$		91.6	$5.3\cdot10^{6}$
$(H_2C{=}CHCOOCH_2)_4C$	473	$7.2\cdot10^{-8}$	7.1	180.6	$1.6\cdot10^{18}$

Notation: n is the number of ester groups in the molecule, E the activation energy, and A the pre-exponential factor. *R = $CH_2OCOCH_2CH_3$.

The formation of radicals via this reaction of cumenyl hydroperoxide with the double bonds in polyacrylic esters has been recently studied.[27] The radicals are formed via the reaction

$$ROOH + XHC{=}CH_2 \rightarrow {}^{\cdot}CHXCH_2OH + RO^{\cdot}.$$

As can be seen from the data presented below, a marked deviation from additivity is observed in this reaction also (at 343 K):

Monomer	Methyl acrylate	Tri(hydroxymethyl)-propane triacrylate	Pentaerythritol tetra-acrylate
k, litre mol^{-1}s^{-1}	$1.75\cdot10^{-7}$	$6.1\cdot10^{-8}$	$2.4\cdot10^{-8}$
$\Delta\Delta G^{\neq}_{ad}$, kJ mol^{-1}	0	3.0	5.6

As can be seen from the examples quoted, the deviation from additivity of the partial rate constants is observed for a wide variety of reactions, namely for the reactions of $RO_2^{\cdot}$ with RH (RH = polyhydric alcohol or polyfunctional ester), of $RO_2^{\cdot}$ with $H_2C{\equiv}CHR$, of O_2 with RH, of O_2 with $H_2C{=}CHR$, and of ROOH with $H_2C{=}CHR$. The model which explains these findings is discussed in the next Section.

V. THE MULTIDIPOLAR MODEL OF THE TRANSITION STATE FOR THE REACTION OF A POLAR SPECIES WITH A POLYFUNCTIONAL MOLECULE

We shall consider the possible causes of the deviation from additivity of the partial rate constants for the reactions enumerated above. Substituents in unsaturated compounds are known to exert a mesomeric effect, which is manifested in those cases where the substituent is located in the α-position with respect to the double bond or when there is a system of conjugated double bonds in the molecule. In the examples quoted above (reactions involving pentaerythritol acrylate esters), the ester groups are separated by several C–C bonds, which completely rules out the mesomeric effect as a cause of the deviation from additivity. Furthermore, the same deviation is observed also in the reactions of aliphatic compounds, where there are no double bonds.

The inductive effect is transmitted via σ-bonds; we shall consider whether it can be the cause of the deviation from additivity. Analysis of the structures of molecules for which the above reactions have been investigated shows that the polar groups in the molecule are separated from the reacting bond (C–H or C=C) by four, six, eight, or more σ-bonds. The inductive effect is known to decay already in the second or third C–C σ-bond and for this reason cannot play any role in all the examples quoted above. It affects only the influence of the polar group nearest to the reaction centre and the appearance of additional groups in the molecule no longer involves their inductive effect.

The steric factor is manifested when a bulky group, in particular, a quaternary carbon atom, is present next to the reaction centre. In the pentaerythritol esters, where the peroxy-radical attacks a C–H bond in the alcohol group, this effect apparently occurs. However, it does not explain the change in the partial rate constant for the reaction involving peroxy-radicals (see the Section about the reactions of $RO_2^{\cdot}$ with esters), since, firstly, when the ester group is replaced by an alkyl group in such esters the steric effect is retained, secondly, on passing from a diester to a tetraester, the rate constant increases (Table 2), while the steric effect should reduce it, and, thirdly, in the reactions of $RO_2^{\cdot}$ with dicarboxylic acid esters and with polyhydric alcohols (Tables 3, 4, and 6) there is no steric hindrance to attack and yet the deviation from additivity does occur.

Thus the three effects examined above do not explain the deviations of the partial rate constants from additivity, which are frequently encountered experimentally. The most probable and possibly the only cause is the effect of the electrostatic interaction of the polar groups in the molecule and the influence of the field which they generate on the transition state. The point is that, in all the examples examined, the molecule containing functional groups is either attacked by polar species ($RO_2^{\cdot}$, ROOH) or forms a polar transition state, as in the reactions involving oxygen. Evidently the attack of a polar species on a polyfunctional molecule is accompanied by an electrostatic interaction, whose energy depends on the dipole moments and the disposition of these groups.

These simple considerations were used as the basis for the concept of the multidipolar interaction in the reactions of polyfunctional compounds.[6] From the standpoint of electrostatic interactions, a polyfunctional molecule constitutes a multidipole, i.e. a set of interacting dipoles. We shall consider such a molecule, containing n functional groups, as a set of interacting dipoles with dipole moments μ_1, μ_2, ..., μ_n. These dipoles rotate as a result of the rotation of the molecular fragments, but they cannot assume any arbitrary mutual orientation, because their rotation is limited by the condition that the valence angles and the internuclear distances in the molecule remain constant.

Thus a polyfunctional molecule considered in this way consists of a semirigid skeleton made up of atoms in which groups (dipoles) having a limited mobility are located at specific sites. If the polar groups are separated by several C–C bonds (two and more), then the distance between the centres of the dipoles will exceed the length of each group (dipole). The energy of the interaction of such dipoles can be described with an adequate approximation by the formula for the interaction of two point dipoles:[28]

$$U_{ij}\ (\text{kJ mol}^{-1}) = 60\,(\mu_i\mu_j N_A/\varepsilon r_{ij}^3)\,[\sin\theta_i \sin\theta_j \cos(\varphi_j - \varphi_i) - 2\cos\theta_i \cos\theta_j] \quad (1)$$

where N_A is the Avogadro number, ε the dielectric constant of the medium, θ_i and θ_j are the angles of inclination of the polar axes of the dipoles i and j relative to the line connecting their centres, and ϕ_i and ϕ_j are the angles between the polar axes of the dipoles and the perpendicular lines drawn through their centres; μ is expressed in Debyes (D) and r in Ångstroms (Å). The energy of the interaction at the dipoles is correspondingly equal to the sum of the energies of the pair interactions ($i \neq j$):

$$U_n = \frac{1}{2}\sum_i \sum_j U_{ij} \ . \quad (2)$$

In order to estimate the value which the energy of such an interaction can assume, we shall consider several examples. Suppose that $\varepsilon = 1$, that all the dipolar groups have a dipole moment of 2 D, and that all the r_{ij} are also equal.

(1) If $n = 2$ and $r = 3$ Å, then $U_{\min} = -18$ kJ mol^{-1} and $U_{\max} = 18$ kJ mol^{-1}.

(2) If $n = 2$ and $r = 4$ Å, then $U_{\max} = 7.5$ kJ mol^{-1}.

(3) If $n = 3$, $r = 4$ Å, and the dipoles are located at the vertices of a triangle, then $U_{\max} = 20$ kJ mol^{-1}.

(4) If $n = 4$, $r = 4$ Å, and the dipoles are located at the vertices of a square, then $U_{\max} = 28$ kJ mol^{-1}.

The activation energy for radical abstraction reactions varies in most cases in the range from 10 to 60 kJ mol^{-1}. Consequently the energy of the dipole–dipole interaction is comparable to the activation energy for radical reactions. When a molecule of this kind is attacked by a species having a dipole moment, a conglomerate consisting of $n + 1$ dipoles arises in the transition state, which also represents a set of point dipoles, the interaction energy of which is described by the expression

$$U_{n+1} = \frac{1}{2}\sum_i^{n+1} \sum_j^{n+1} U_{ij} \ . \quad (3)$$

The contribution of the multidipolar interaction to the Gibbs free energy of activation is

$$\Delta G_\mu^{\neq} = N_A\,(U_{n+1} - U_n) \ . \quad (4)$$

If the mutual orientations of the polar groups of the molecules and the distances between them are similar in the initial and transition states, we obtain

$$\Delta G_\mu^{\neq} = \frac{N_A \mu^*}{\varepsilon} \sum_i^n \frac{\mu_i}{r_i^3} f(\theta^*, \theta_i, \varphi^*, \varphi_i) \ , \quad (5)$$

where the asterisk refers to the polar group of the attacking species. The component of the Gibbs free energy of activation $\Delta G_\mu^{\neq}$, due solely to the dipole–dipole interaction, is defined by the simple relation[29]

$$\Delta G_\mu^{\neq} = RT \ln (k_0/k) \ . \quad (6)$$

The difference between the energies of the multidipolar interaction in the transition state and in the initial molecule may be both positive and negative. A monofunctional compound can be used as a reference. In this case k_0 already takes into account the dipole–dipole interaction and the formula $\Delta G_\mu^{\neq} = RT \ln (k_0/k)$ reflects the influence of the multidipolar interaction after the subtraction of the interaction of the attacking species with the field of the attacked reaction centre (the dipole–dipole pair interaction).

The relation between $\Delta G_\mu^{\neq}$ and the experimental activation energy E and the experimental pre-exponential factor A can be found in the following way. Since $E = RT^2 \mathrm{d}\ln k/\mathrm{d}T$ and $\ln k = \ln k_0 - \Delta G_\mu^{\neq}/RT$, we obtain

$$E = E_0 + \Delta G_\mu^{\neq} - T\mathrm{d}\Delta G_\mu^{\neq}/\mathrm{d}T \ . \quad (7)$$

The temperature dependence of E is due to two factors. Firstly, $\Delta G_\mu^{\neq} = \Delta G_{\mu 1}^{\neq}/\varepsilon$; the dielectric constant ε varies with temperature in accordance with the exponential function

$$\varepsilon = \varepsilon_0 e^{-L_\varepsilon T} \ .$$

Secondly, the extent of the rotation of the molecular fragments and the amplitude of the deformation vibrations of the bonds increase with increase of temperature. The mutual orientation of the dipoles is correspondingly averaged out and $\Delta G_{\mu 1}^{\neq}$ diminishes.

If the molecule is regarded as a microdielectric, one can assume that $\Delta G_{\mu 1}^{\neq}$ is related to temperature (like ε) in the following way:

$$\mathrm{d}\ln \Delta G_{\mu 1}^{\neq}/\mathrm{d}T = -L_G \ .$$

After substitution of the expressions for $\Delta G_\mu^{\neq}$ in Eqn.(7) and differentiation, we obtain

$$E = E_0 + \Delta G_\mu^{\neq} + T\,(L_G - L_\varepsilon)\,\Delta G_\mu^{\neq} \ .$$

Since the entropy is linked to the Gibbs free energy by the relation $\Delta S = -\mathrm{d}\Delta G/\mathrm{d}T$, we obtain for the change in the activation entropy as a result of the multidipolar interaction

$$\Delta S_\mu^{\neq} = -\mathrm{d}\Delta G_\mu^{\neq}/\mathrm{d}T = (L_G - L_\varepsilon)\,\Delta G_\mu^{\neq} \ . \quad (8)$$

On the other hand, $\Delta S_\mu^{\neq}$ can be estimated from the pre-exponential factor: since $\Delta S^{\neq} = R \ln A + \text{const.}$, we obtain

$$\Delta S_\mu^{\neq} = R \ln (A/A_0) \ . \quad (9)$$

Using Eqns.(7)–(9), we have

$$\Delta G_\mu^{\neq} = \frac{E - E_0}{1 + \ln (A/A_0)/\ln (k_0/k)} \ , \quad (10)$$

$$L_G = L_\varepsilon + T^{-1}[\ln (A/A_0)/\ln (k_0/k)] \ . \quad (11)$$

The conclusions which follow from the model of the multidipolar transition state examined above are compared with the experimental data in the next Section.

The influence of polar groups on the energy of the transition state partly resembles solvation, but there are two significant differences. Firstly, solvent molecules approach closely the polar transition state (reaction centre) and surround it, whereas the polar groups of the polyfunctional molecule exert their influence via a field over a certain distance. Secondly, the molecules solvating the polar group (including the reaction centre) are oriented in the energetically most favourable manner, whereas the orientation of the groups in a polyfunctional molecule is restricted by the specific disposition of the atoms and groups in it.

The dipole–dipole interaction can also exert a more profound influence on the transition state, apart from establishing a specific electrostatic potential. If readily polarisable bonds (π-bonds, atoms with p and d electrons), which are polarised in the transition state, participate in the reaction, then the polar groups in the molecule can influence the polarisation of the transition state, which can lead to an intensification of the effect of the multidipolar interaction and to a greater deviation from additivity. Finally, in those cases where the reaction proceeds with electron transfer and in the transition state a neutral species is converted into an ion (ion pair), the result should be a stronger and longer-range ($U \propto r^{-2}$ instead of $U \propto r^{-3}$) ion–dipole interaction and correspondingly a higher value of $|\Delta G_{\mu}^{\neq}|$.

VI. ANALYSIS OF EXPERIMENTAL DATA WITHIN THE FRAMEWORK OF THE CONCEPT OF THE MULTIDIPOLAR INTERACTION IN THE TRANSITION STATE

It follows from the model of a polyfunctional molecule as a system of interacting groups (dipoles) that, in those cases where such a molecule is attacked by a non-polar species, the ion–dipole interaction potentials in the molecule and in the activated complex are the same or very similar, so that the rule of the additivity of the partial rate constants should hold. As we have seen, the rule breaks down for the reactions of $RO_2^{\cdot}$ with a series of esters of pentaerythritol and its analogues (Table 2).

The rate constants for the reactions of trichloromethyl radicals with these esters have been measured.[30] The reactions were investigated in CCl_4 at 373 K using benzoyl peroxide as the initiator. It was continued until the consumption of the peroxide was complete. The amounts of chloroform and hexachloroethane formed were determined by gas–liquid chromatography. The reactions taking place in the initiator (I)–ester (RH)–CCl_4 system are described by the following scheme:

$$I \xrightarrow{k_d} \dot{r} + \dot{r} \xrightarrow{k_t} 2\dot{r},$$
$$\dot{r} + CCl_4 \rightarrow rCl + \dot{C}Cl_3,$$
$$\dot{C}Cl_3 + RH \xrightarrow{k_p} CCl_3H + \dot{R},$$
$$\dot{R} + CCl_4 \rightarrow RCl + \dot{C}Cl_3,$$
$$\dot{C}Cl_3 + \dot{C}Cl_3 \xrightarrow{k_t} C_2Cl_6.$$

According to this scheme, the amount of hexachloroethane formed at the end of the experiment corresponds to the amount of free radicals produced on decomposition of benzoyl peroxide. The reaction has a chain mechanism and the average chain length varies from 3 to 40 units. The rate constant ratio $k_p(2k_t)^{-1/2}$ was determined from the amount of $CHCl_3$ formed. The absolute value of k_p was calculated on the assumption that $2k_t = 3.1 \times 10^9$ litre mol^{-1} s^{-1}.[31] The experimental conditions and the values of $k_p(2k_t)^{-1/2}$ and k_p are listed in Table 9. The results make it possible to calculate and compare the partial rate constants for the reactions of dichloromethyl radicals with the $-CH_2OCOCH_2CH_3$ fragment for different numbers of ester groups in the molecule.

It is seen from the data in Table 9 that the k_p calculated per fragment are close for all three propionates regardless of the number of ester fragments in the molecule. Thus, to a first approximation, the rule of additivity holds for the reactions of trichloromethyl radicals with polyfunctional esters. The trichloromethyl radical is an electrophilic species, like the peroxy-radical. When the inductive effect is a possible cause of the deviation from additivity, such deviation would therefore have been observed also for the $\dot{C}Cl_3$ radicals, as happens for peroxy-radicals. The validity of the rule of additivity for radicals in the case of $\dot{C}Cl_3$ demonstrates that in this instance the inductive effect does not play a significant role. The transition state in the case where a C–H bond is attacked by $\dot{C}Cl_3$ apparently has a low dipole moment, which does not exceed 0.5 D. The energy of the interaction of the ester groups in such a dipole is low and its effect on k_p is within the limits of the accuracy of the measurement (for comparison, we may recall that the dipole moment of the peroxy-radical is ~2 D). An analogous result has been obtained for the reactions of non-polar undecyl radicals with monoesters and polyesters[11] (Table 10). The reactivity of the esters has been investigated by the method of competing reactions:

$$C_{11}H_{23}^{\cdot} + RH \xrightarrow{k_1} C_{11}H_{24} + R^{\cdot},$$
$$C_{11}H_{23}^{\cdot} + O_2 \xrightarrow{k_2} C_{11}H_{23}OO^{\cdot}.$$

Table 9. The rate constants for the reactions of trichloromethyl radicals with esters (373 K, CCl_4).[30]

Ester	$10^3 k_p(2k_t)^{-1/2}$, litre$^{1/2}$mol$^{-1/2}$s$^{-1/2}$	k_p, litre mol^{-1}s^{-1}	k_p/n, litre mol^{-1}s^{-1}
$C(CH_2OCOCH_2CH_3)_4$	2.8±0.1	160	40
$C[CH_2OCO(CH_2)_8CH_3]_4$	22.3±0.4	1250	—
$(CH_3)_2C(CH_2OCOCH_3)_2$	1.8±0.1	100	50
$CH_3CH_2C(CH_2OCOCH_2CH_3)_3$	3.1±0.5	170	43

The source of undecyl radicals was dilauryl peroxide, which was decomposed in chlorobenzene in the presence of the ester RH in an atmosphere of oxygen. The intensity of the first reaction was inferred from the yield of undecane relative to the decomposed peroxide. Table 10 shows that the relative rate constants for the reactions of the alkyl radical with the esters calculated per group differ by not more than 15%.

Table 10. The rate constants for the reactions of undecyl radicals with esters (373 K, C_6H_5Cl).[11]

Ester	$10^4 (k_1/k_2)$	$10_4 (k_1/nk_2)$
$CH_3(CH_2)_4COOCH_3$	1.1	1.1
$CH_3OCO(CH_2)_8COOCH_3$	1.8	0.9
$CH_3(CH_2)_4COOCH(CH_3)_2$	1.2	1.2
$(CH_3)_2CHOCO(CH_2)_8COOCH(CH_3)_2$	2.2	1.1
$CH_3(CH_2)_3COOCH_2CH_3$	1.3	1.3
$[CH_3(CH_2)_3COOCH_2]_4C$	6.8	1.7

The deviation of the partial rate constants from additivity is thus observed only in those cases where the molecule is attacked by polar species ($RO_2^{\cdot}$, ROOH) or when a polar transition state is formed (in reactions with O_2). It follows from Eqn.(4) that the component $\Delta G_{\mu}^{\neq}$ due to the dipole–dipole interaction can be both positive when $U_{n+1} > U_n$ and negative when $U_{n+1} < U_n$, i.e. the deviations from additivity can be both towards a decrease and an increase of the reaction rate constant compared with the sum of the partial rate

constants. Indeed both cases have been observed experimentally (Table 11), but there are more examples with $\Delta G_{\mu}^{\neq} > 0$.

Table 11. The sign of the multidipolar effect ($\Delta G_{\mu}^{\neq}$) in various radical reactions.

Radical*	Molecule	Sign
$C_6H_5(CH_3)_2COO^{\cdot}$	$ROCO(CH_2)_nCOOR$	+
$C_6H_5(CH_3)_2COO^{\cdot}$	$ROCO(CH_2)_2COOR$	+
$C_6H_5(CH_3)_2COO^{\cdot}$	$ROCO(CH_2)_2O(CH_2)_2COOR$	+
$C_6H_5(CH_3)_2COO^{\cdot}$	$(CH_3)_{4-n}C(CH_2OCOCH_2CH_3)_{n-4}$	−
$C_{16}H_{35}OO^{\cdot}$	$HOCH_2(CH_2)_nCH_2OH$	+
$C_{16}H_{35}OO^{\cdot}$	$R_{4-n}C(CH_2OH)_n$	−
$RO_2^{\cdot}$	$HOCH_2(CH_2)_nCH_2OH$	+
$RO_2^{\cdot}$	$R_{4-n}C(CH_2OH)_n$	−
$C_6H_5(CH_3)_2COO^{\cdot}$	$R_{4-n}C[CH_2OCOC(CH_3)=CH_2]_n$	+
O_2	$C[CH_2OCOC(CH_3)=CH_2]_4$	+
$C_6H_5(CH_3)_2COOH$	$C[CH_2OCOHC=CH_2]_4$	+

*Here $RO_2^{\cdot}$ is the radical derived from diethylene glycol dicaprylate.

It follows from Eqns.(4) and (5) that $\Delta G_{\mu}^{\neq}$ is lower the further is the reaction centre from the polar groups. This conclusion has been tested in relation to the reactions of $RO_2^{\cdot}$ with pentaerythritol esters.[14] In the molecule of such an ester the radical $RO_2^{\cdot}$ attacks both the C–H bonds of the alcohol residue, located near the ester groups, and the C–H bonds of the acid residue. The greater the number of CH_2 groups in the acid residue, the greater the contribution of the CH_2 groups remote from the polar ester groups to the overall reaction rate constant. With increase of the number of methylene groups in the acid residue of the ester, the rate constant calculated per CH_2 group should therefore appraoch that of an n-paraffin, which has in fact been confirmed by experimental data:[14] $k_{CH_2} = 1.4$ litre mol^{-1} s^{-1} (407 K) for pentaerythritol tetrapropionate, 2.7 litre mol^{-1} s^{-1} for pentaerythritol tetracaprate, and 2.8 litre mol^{-1} s^{-1} for n-heptadecane. It is seen that, with increase in the number of CH_2 groups, the deviation from additivity diminishes as the distances of the attacked group from the dipolar groups are increased.

Table 12. The parameters* of the multidipolar interaction in the reactions of cumenylperoxy-radicals with the esters of mono- and di-carboxylic acids.[4]

Ester	k (413 K)	$\Sigma k_{pl}^{\sim}$	$\Delta G_{\mu}^{\neq}$, from Eqn.(6)	E	lg A	$\Delta G_{\mu}^{\neq}$, from Eqn.(10)	$\Delta S_{\mu}^{\neq}$	L_G
$CH_3CH_2COOCH_3$	92	—	—	29	5.63	—	—	—
$CH_3(CH_2COOCH_3)_2$	7.2	185	11.1	69	9.58	11.8	76	9.3
$CH_3CH_2COOC_2H_5$	18	—	—	37	5.93	—	—	—
$CH_3(CH_2COOC_2H_5)_2$	7.0	37	5.6	69	9.57	6.0	70	14.4
$CH_3CH_2COOC(CH_3)_3$	8.9	—	—	53	7.65	—	—	—
$CH_3[CH_2COOC(CH_3)_3]_2$	2.6	185	6.6	73	9.65	5.7	38	9.6

*k and A are expressed in litre mol^{-1} s^{-1}, E and $\Delta G_{\mu}^{\neq}$ in kJ mol^{-1}, and $\Delta S_{\mu}^{\neq}$ in J mol^{-1} K^{-1}.

Table 12 presents the values of E and lg A for the reactions of peroxy-radicals with monoesters and polyfunctional esters. In all the cases quoted, the compensation effect is observed: with increase of the activation energy, the pre-exponential factor also increases. The concept of the multidipolar interaction explains this effect; within its framework, the effect is characterised by the coefficient L_G [see Eqns.(7)–(11)]. The physical significance of this compensation consists in the fact that, owing to the intensification of the torsional and deformation vibrations of the groups in the molecule as the temperature rises, the value of $|\Delta G_{\mu}^{\neq}|$ decreases.

Table 12 shows that the $\Delta G_{\mu}^{\neq}$ obtained by two different methods agree satisfactorily. Since the manifestation of the effect of the multidipolar interaction requires as an obligatory condition that one of the reactants should contain several polar groups, it follows that the effect should also appear when a radical containing several polar groups interacts with the polar molecule. Data of this kind have been obtained in the studh of the kinetics of the oxidation of mono- and tetra-functional unsaturated esters in the presence of ionol as the inhibitor. The rate constant for the reaction of peroxy-radicals with ionol was calculated from the experimental data (Table 13). They show that the peroxy-radical containing four ester groups attacks ionol ~4 times more slowly than one having a single ester group; $\Delta G_{\mu}^{\neq} \cong 4$ kJ mol^{-1}. The fact that in this instance the above difference is caused by the dipole–dipole interaction has been confirmed by experiments on the coupled oxidation of the same esters with cumene, from which the rate constants for the reactions of the same peroxy-radicals with the weakly polar cumene were obtained ($\mu = 0.4$ D for cumene and 1.6 D for ionol). The data in Table 13 show that the rate constants for the reactions of the above radicals with the non-polar cumene are very similar.

Table 13. The rate constants for the reactions of mono- and poly-functional peroxy-radicals of monomers with ionol (k_2, 323 K) and cumene (k_1, 343 K).

Monomer	k_1, litre $mol^{-1}s^{-1}$	k_2, litre $mol^{-1}s^{-1}$	$\Delta G_{\mu}^{\neq}$, kJ mol^{-1}
$CH_3OCOHC=CH_2$	1.2	$8.1\cdot10^3$	—
$(H_2C=CHCOOCH_2)_4C$	1.0	$1.9\cdot10^3$	4.1
$CH_3OCO(CH_3)C=CH_2$	0.7	$3.8\cdot10^3$	—
$[H_2C=C(CH_3)COOCH_2]_4C$	0.8	$1.1\cdot10^3$	3.5

The important factor is the heat of reaction, on which depends not only the activation energy but also the configuration of the activated complex. According to Hammond's postulate,[2] the configuration is closer to that of the reaction products the more endothermic the reaction. In its turn, the higher the heat of reaction, then, other conditions being equal, the weaker the reflection of the structural factors in the reaction rate constant. We shall consider how this tendency is manifested in the reactions of polyfunctional molecules. The comparison can be carried out for peroxy-radicals, hydroperoxide, and oxygen in their reactions with unsaturated compounds. The dipole moments of $RO_2^{\cdot}$ and ROOH are similar and oxygen, having added to the double bond, also produces a peroxy-radical. On the other hand, these reactants differ sharply in their reactivities, which can be seen from a comparison of the rate constants for the

above reactions. The reactions and the values of ΔH^0 calculated for them are presented below (on the basis of the data in Kondrat'ev's handbook[7]):

$$CH_3OO^{\cdot} + H_2C{=}CH_2 \rightarrow CH_3OOCH_2\dot{C}H_2 \quad (\Delta H^0 = -46 \text{ kJ mol}^{-1});$$
$$CH_3OOH + H_2C{=}CH_2 \rightarrow CH_3O^{\cdot} + HOCH_2\dot{C}H_2 \quad (\Delta H^0 = 30 \text{ kJ mol}^{-1});$$
$$O_2 + H_2C{=}CH_2 \rightarrow {}^{\cdot}OOCH_2\dot{C}H_2 \quad (\Delta H^0 = 130 \text{ kJ mol}^{-1}).$$

The peroxy-radicals also differ in their reactivities in addition reactions: the $RO_2^{\cdot}$ derived from styrene is much more reactive than the $RO_2^{\cdot}$ derived from acrylates. The rate constants from the values of ΔH^0 and $\Delta G_{\mu}^{\neq}$ in reactions involving addition to the double bond in tetra-acrylate esters are compared below:

Reactant	$RO_2^{\cdot}$(styrene)	$RO_2^{\cdot}$(acrylate)	$C_6H_5(CH_3)_2COOH$	O_2
T, K	323	323	343	343
k, litre mol^{-1}s^{-1}	101	0.8	$2.4\cdot10^{-6}$	$4\cdot10^{-10}$
ΔH^0, kJ mol^{-1}	−46	—	30	130
$\Delta G_{\mu}^{\neq}$, kJ mol^{-1}	0.5	1.2	5.6	13.8

Evidently the effect of the multidipolar interaction is indeed manifested in the above series of reactions to a greater extent the more endothermic the reaction.

We have seen that the energy of the dipole–dipole interaction depends on the dipole moment of the species, their orientation, and the distance between them. For a distance of 4 Å and a dipole moment of 2 D, the absolute differences between the interaction potentials are $|U_{N+1} - U_n|_{max} = 12.5$ kJ mol^{-1} ($n = 2$) and 8 kJ mol^{-1} ($n = 3$), as shown above. Thus the maximum energy of the multidipolar interaction is ~10 kJ mol^{-1} and $\Delta G_{\mu}^{\neq}$ can vary in the range from 0 to 10 kJ mol^{-1}. The data presented in Tables 4, 6, 7, 8, 12, and 13 show that the $\Delta\Delta G_{ad}^{\neq}$ do not as a rule exceed 10 kJ mol^{-1} and in most cases are in the range from 2 to 4 kJ mol^{-1}. There is only one exception: the data for the reactions of oxygen with esters of mono- and di-carboxylic acids (Table 8), where $\Delta\Delta G_{ad}^{\neq} = 25$ kJ mol^{-1}. This enormous difference between the rate constants is clearly outside the framework of the effect of the multidipolar interaction and its cause remains obscure.

For the reactions of unsaturated compounds with oxygen (Table 8) and a hydroperoxide, the $\Delta\Delta G_{ad}^{\neq}$ (7 and 5 kJ mol^{-1}) are apparently higher than the $\Delta G_{\mu}^{\neq}$ determined solely by the interaction of these groups as rigid dipoles (in these reactions the distance of the reaction centre from the ester groups is 5–6 Å and the energy of the dipole–dipole interaction is in this instance 2–3 kJ mol^{-1}). However, only a readily polarisable π-bond is involved in the above reaction; the polarisation of this bond contributes to $\Delta G^{\neq}$ and the observed $\Delta\Delta G_{ad}^{\neq}$ apparently includes both the energy of the electrostatic interaction of the dipolar groups and the difference between the polarisations of the reacting bond under the influence of the polar groups in mono- and poly-functional esters. One cannot rule out also a longer-range ion–dipole interaction when the reactions take place with electron transfer via the activated complexes $O_2^{\ddot{-}}...\dot{C}H_2{-}\overset{+}{C}OOR$ and $ROOH^{\ddot{-}}...\dot{C}H_2{-}\overset{+}{C}OOR$.

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Thus the extensive experimental data for the reactions of $RO_2^{\cdot}$, ROOH, and O_2 with saturated and unsaturated polyesters as well as the reaction of the polyfunctional radical $RO_2^{\cdot}$ with ionol show convincingly that the deviations from additivity are in almost all cases a consequence of the electrostatic interaction of the polar groups as a set of dipoles. In the case of unsaturated compounds this effect is enhanced by the influence of the polar groups on the polarisation of the π-bonds in the transition state.

As shown above, the effect of the multidipolar interaction is characteristic of the reactions of polyfunctional compounds and apparently plays an important role in the reactions of polymers containing functional groups and biopolymers.

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