Translated from *Uspekhi Khimii*, 47, 1119-1143 (1978) U.D.C. 541.124/.128:541.124-16

Effect of Mobility of Medium on Formal Kinetics of Chemical Reactions in a Condensed Phase

O.N.Karpukhin

Chemical kinetics is examined under conditions such that the medium is quite mobile (classical kinetics), when it can be regarded as immobile throughout the process (i.e. with kinetic non-equivalence of reactant species), and also under intermediate conditions of kinetic non-equivalence maintained only during the lifetime of the leading active species. Methods for studying the kinetics of variation in reactivity due to change in the local properties of the medium are discussed, and reasons for the levelling of reactivity in a series of structurally different molecules on passing from liquid to solid media are analysed. The bibliography contains 37 references.

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I. INTRODUCTION

In a condensed phase every species is subject to the time-variable influence of the surrounding molecules of the medium. This affects the probability of occurrence of primary steps of chemical conversion. Herein lies the chief cause of the qualitative difference between a primary chemical step in a condensed phase and the corresponding step in the gas phase. In the study of, for instance, a bimolecular reaction in the latter it is sufficient to examine the interaction of the two reactants in a vacuum, for the remaining species have no appreciable effect on this process.

A substantially different situation obtains in a condensed phase, in which molecules of the medium influence all stages of chemical interaction. The properties of the molecules govern transport of reactant species towards each other and the probability of their meeting. The medium has a considerable effect also on the actual chemical reaction: surrounding molecules may prevent rearrangement of reactant species, the electromagnetic field due to the medium changes the relation between different possible primary reaction paths, and considerable exchange of energy takes place between medium and reactants. Thus the medium plays a part in organising the primary step of chemical conversion[1]. The molecular motion of the medium produces continuous change in its local properties in the immediate environment of the reactants. The formal kinetics of a chemical process depends on the rapidity of variation in these local properties influencing the reactivity of the reactants.

The present Review examines the influence of the dynamics of the variation in these local properties of the medium on the kinetics of a chemical process, and discusses qualitative differences between the description of reaction kinetics in a condensed medium and the classical kinetics of gas-phase reactions. The problem of which local properties cause the variation in reactivity is almost completely ignored. Nor are more complicated aspects of the influence of the medium on chemical kinetics considered (the structure and the reasons for the formation of more or less stable complexes of the reactants with the medium, or solvate sheaths, the influence of the supermolecular structure of the medium on the process, etc.). Consequently the Review regards a condensed phase as a macroscopically homogeneous medium, non-uniformity in which can arise only at a cellular level, i.e. at distances of the order of the dimensions of the reactant molecules.

II. FORMAL KINETICS OF REACTIONS IN A CONDENSED PHASE

Two main approaches are usually made to the kinetics of chemical reactions in the gas phase. If the process is sufficiently slow, the reactants have enough time to exchange energy with the medium, so that they are in a nearly equilibrium distribution with respect to energies, rates, and distances apart. Under these conditions the law of mass action is used to describe the formal kinetics: the rate of a given primary process is proportional to the product of the reactant concentrations. The coefficient of proportionality is a measure of the rate constant; its temperature dependence is given by the Arrhenius equation.

In the other extreme case, in which chemical interaction produces either a chemically unstable species or a highly reactive species, i.e. one that undergoes further chemical changes only through several collisions with other molecules, the kinetic description is based neither on the law of mass action nor on the concept of the reaction rate constant but on the probability of involvement of the species in a particular reaction after its formation.

In a condensed phase the probability of chemical reaction may be influenced not only by the properties of the reactants but also by the local properties of the medium. In general, therefore, the rate constant of a chemical reaction occurring in a condensed phase is a function of some parameter u representing such local properties. We shall not now specify the physical nature of u, since various media may have different effects on various primary chemical processes. The parameter may represent the formation of specific complexes, the effect of the electromagnetic field of the medium, steric hindrance, direct involvement of molecules of the medium in

the chemical reaction. In general, if the local properties governing the probability of chemical reaction depend on several parameters, u is a vector.

On the above approach the kinetics of the variation in the macroscopic concentration of a substance A involved e.g. in a simple unimolecular reaction is described by the integrodifferential equation

$$\frac{d[A]}{dt} = \int \frac{dA(u)}{dt} du = \int k(u) A(u) du, \quad (1)$$

where $A(u)$ is the distribution function of the concentration of A in terms of the parameter u, and $k(u)$ is a function relating the effective rate constant of chemical conversion of A to u. Equation (1) leads to the usual exponential law of variation of [A], known as the first-order kinetic equation, in only two cases—(i) if the rate constant varies little with the local properties of the medium, i.e. if

$$k(u) = \text{const}, \quad (2)$$

and (ii) if these local properties vary so rapidly in comparison with the rate of chemical reaction that $k(u)$ can be replaced throughout the process by a mean value and removed from the integral on the right-hand side of Eqn. (1).

Thus the rate of variation in the local properties of the medium, i.e. the relationship between three temporal parameters—the characteristic time of chemical conversion τ_x, the lifetime of the active centre effecting the process τ_e, and the correlation time between the reactants over all states in the medium τ_c—must be taken into account in order to describe the kinetics of a process in a condensed phase. Here τ_x is a macroscopic parameter of the process, representing the time for significant change in composition of the reactants; it can be characterised by the reciprocal of the relative rate of change in concentration of the reactants. For a unimolecular reaction τ_x is then the reciprocal of the rate constant k_1:

$$\tau_x = 1/k_1,$$

For a bimolecular reaction it is given by the reciprocal of the product of the rate constant k_2 and the instantaneous concentration c:

$$\tau_x = 1/k_2 c.$$

The quantity τ_e may represent the time from the instant of formation of an active centre until its destruction or conversion into another active centre. For molecular decomposition τ_e is of the order of the time of rearrangement of the molecule during decomposition, i.e. the vibration period of the atoms in the molecule. It will be considerably longer when the molecule breaks down into active species, e.g. radicals. Thus for radicals that have escaped into the bulk of the specimen

$$\tau_e = 1/k_t [R],$$

where k_t is the rate constant of such loss. The lifetime of an oxidation chain may also correspond to τ_e:

$$\tau_e = 1/\sqrt{w_i k_t},$$

where w_i is the rate of formation of active centres in the system. Different values of τ_e may apply to different primary steps in the same composite process. For example, τ_e is considerably shorter for active centres that recombine in the cage in which they were formed than for those that have escaped from the cage and recombine in the bulk of the specimen.

The correlation time τ_c between species in a medium is the time during which a reactive species is able to exist in all possible states in which it has different reactivities. It is determined by how rapidly those properties of the reactant species that determine reactivity change as a result of the relative motion of the species and the molecules of the medium. The magnitude of τ_c can be judged to some extent from the correlation time of a paramagnetic probe or the time of depolarisation of luminescence. There is some analogy between τ_c and the time of establishment of thermal equilibrium between the species and the medium. In this sense we can speak of a correlation time even in gas-phase systems. Since energy is exchanged in the gas phase by collisions between particles, the correlation time for energy is of similar order of magnitude to the time between two collisions. In a condensed phase any particle is almost always in a state of collision with some particle of the medium, and τ_c is then very short—around a few picoseconds—for energy. Correlation times with other characteristics of reactant species therefore have greater practical value.

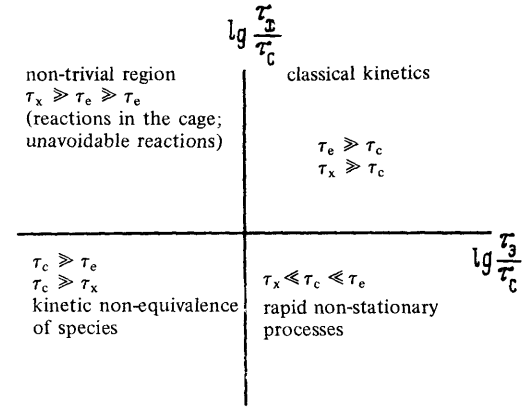


Figure 1. Qualitative variation in kinetics of chemical processes with the relationship between the characteristic times of their occurrence and the correlation time of the species in the medium.

The formal kinetics of chemical processes are qualitatively different depending on the relationship between the above three characteristic times. If in a plane $\lg(\tau_e/\tau_c)$ is plotted as abscissa, and $\lg(\tau_x/\tau_c)$ as ordinate (Fig. 1), every specific chemical process can be represented by a point in this plane†. The upper right-hand corner contains processes for which the correlation time is the shortest of the three:

$$\tau_c \ll \tau_x; \ \tau_c \ll \tau_e. \quad (3)$$

† The three characteristic times (primarily τ_x) may vary during change in the composition of the system due to the chemical process. In the plane, therefore, the chemical reaction is represented by a segment of a curve. For the sake of simplicity, however, we shall henceforward neglect the linear dimensions of this segment: more precisely, we shall consider only those processes during which change in the relation between the characteristic times is insignificant.

All the primary steps then occur under the same conditions, so that the kinetic description is formally analogous to that in the gas phase. The effective rate constants of the primary reactions will equal the average values of the primary constants over all possible values of u realisable in the given medium under the given conditions. This part of the coordinate plane is the region in which all the classic concepts of chemical kinetics are valid.

The lower left-hand corner contains processes for which the correlation time is the longest of the characteristic times:

$$\tau_c \gg \tau_x;\ \tau_c \gg \tau_e. \tag{4}$$

This means that the process occurs as if in a completely "frozen" medium, with the reactant species under unchanged conditions throughout the process, but these conditions may differ for different species, so that the species may be kinetically non-equivalent. Under these conditions the rate of a chemical process is not proportional to the macroscopic concentration of the reactant species, but depends on how the latter are initially distributed with respect to the parameters determining their reactivity in the condensed medium, and how this distribution varies with time. The kinetics of such processes are often termed *polychromatic*[2], since, in contrast to the usual monochromatic processes, the rate of each primary reaction is then defined not by a single rate constant but by a set of rate constants governed by the local conditions. Since the medium is "frozen", the condition of each species remain unchanged throughout the process: i.e. it appears to "remember" its conditions when the process began. The equations of classic kinetics then describe not the variation in the macroscopic concentration of the reactants but that of the density of distribution among various local conditions $A(u)$.

In the above example of a unimolecular reaction $k(u)$ may differ for different $A(u)$ functions. The kinetics of the variation in $A(u)$ will therefore be described for each value by the exponential relation

$$A(u) = A(u)_0 e^{-k(u)t}, \tag{5}$$

but the exponent will differ for different values of u. The variation in the macroscopic concentration of the substance A, given by the equation

$$[A] = \int A(u)_0 e^{-k(u)t}\,du \tag{6}$$

may thus not be exponential in character. A common feature of reactions under these conditions (4) is the kinetic non-equivalence of species of the same chemical structure, which remains unchanged throughout the process.

As we move upwards from the lower left-hand corner of the plane (Fig. 1), we may enter a range of processes in which τ_x is comparable with τ_c. In describing them we must bear in mind that the density of distribution of concentration may vary with u as a consequence not only of chemical change but also of the mobility of the medium. In the case of a unimolecular reaction the kinetics of the variation in $A(u)$ will thus be determined by a more complicated equation than if the law of mass action were formally obeyed:

$$\frac{dA(u)}{dt} = -k(u)A(u) + \frac{\partial A(u)}{\partial u}\frac{\partial u}{\partial t}. \tag{7}$$

Under these conditions it is obviously not always possible to obtain an exponential variation of $A(u)$ with time.

Still higher, in the top left-hand corner of the plane, are situated processes for which the correlation times have intermediate values:

$$\tau_x \gg \tau_c \gg \tau_e. \tag{8}$$

When condition (8) is satisfied, the process takes place under a peculiar quasi-stationary régime. Any reactant species may initiate chemical conversion independently of its state at the start of the process: i.e. the rate of variation of the macroscopic concentration of a reactant, as in classical kinetics, is proportional to its instantaneous macroscopic concentration.

Another large region comprises complicated processes for which $\tau_x < \tau_e$. They lie on the plane to the right and below the 45° line through the origin. This is a region of so called non-stationary processes, for which the lifetimes of the active centres are comparable with the times required for large degrees of conversion. Certain branched-chain reactions can evidently be included here. The present Review will not discuss processes of this kind: it may merely be noted that, when the relations between the characteristic times correspond to the lower half of the plane, their description must allow for the possible kinetic non-equivalence of the reactant species.

III. KINETICS WITH COMPLETE KINETIC NON-EQUIVALENCE OF REACTANT SPECIES

Under conditions such that reactant species of the same chemical structure are completely equivalent kinetically ($\tau_c \ll \tau_e$, $\tau_c \ll \tau_x$) the kinetics of a chemical process does not differ fundamentally from that of a gas-phase process, as already mentioned. Departures from classical views arise only in the description of very fast processes, whose rates are controlled by diffusion. Rate constants of such processes vary with time in conformity with Waite's equation[3,4]. However, deviations of this kind occur both in condensed-phase and in gas-phase reactions. Therefore the present Review will not survey the kinetics of such chemical processes, occurring under conditions of actual kinetic equivalence of species.

If the process occurs under the directly opposite conditions, i.e. if the correlation time is much shorter than the other characteristic times, the kinetic description differs qualitatively from that for a gas-phase process, since reactant species of the same chemical structure may be kinetically non-equivalent. It is not altogether a simple matter to realise such a process: on the one hand, it is necessary that the local properties of the matrix should remain unchanged throughout the process: on the other hand, a chemical process is usually caused by some changes in properties in the immediate vicinity of a molecule of the starting material or is due to the transport of reactant species towards each other. These difficulties probably explain why heterogeneous processes at a gas–solid interface were the first to be examined in terms of kinetic non-equivalence: species on a non-uniform solid surface are under kinetically non-equivalent conditions with respect to species arriving from the gas phase and therefore kinetically equivalent.

During the 1930s Ya. B. Zel'dovich, M. I. Temkin, and S. Z. Roginskii made a large number of studies on such chemical reactions, the results of which were summarised in a monograph[5]. They developed mathematical methods for describing the kinetics, and showed how the form of

distribution of reactants among non-equivalence parameters could influence the process, as well as how the form of distribution could be estimated from kinetic data.

Ideas on the kinetic non-equivalence of reactant species involved in macroscopically homogeneous processes were first used in the 1950s to early 1960s to describe the kinetics of the annealing of radiation defects[6,7] and of the loss of free radicals at low temperatures[2,8,9]. The kinetics of such processes could be described in terms of the so called polychromaticity of the rate constant (Section II).

However, the loss of active centres in a solid matrix is not an altogether convenient process for studying the kinetic non-equivalence of reactant species, since the mechanism of their mutual approach is not always entirely clear. For example, a simple mechanism of free diffusion towards one another in the solid polymer cannot be assumed for such large species as macromolecular radicals. Therefore discussion of the kinetic non-equivalence of radicals has been widely accompanied by that of the mechanism of migration of an active centre, e.g. a valence, through a polymer matrix[10], the possible role of relatively simple impurities in this process[11], possible dimensions for microheterogeneities that might explain the observed rules without recourse to ideas on the kinetic non-equivalence of species in a macroscopically homogeneous medium. For example, a model has been suggested involving fluctuations of the free volume in a solid matrix[12]; in fact it could explain the results in terms of the kinetic equivalence of reactant species. Serious consideration has been given also to a model of controlled diffusion of the process in a homogeneous medium[13,14], providing a formally rigorous explanation of the kinetics of the initial stage of loss of free radicals, but yielding overestimates of the radii of interaction between active centres.

The main evidence for kinetic non-equivalence of species in processes of this kind is provided by the peculiar form and the temperature dependence of the kinetic curves for the variation in reactant concentrations. With change in temperature the process almost ceases after not very large changes in reactant concentrations, although no products capable of inhibiting the reaction have accumulated in the system. Nor is such cessation due to the establishment of any equilibrium. Actually, the process is not completely arrested, but undergoes a so called kinetic termination. The semi-logarithmic form of the kinetic curve, with $[A]/[A]_0$ plotted against $\ln t$, is a straight line extending to high degrees of conversion.

The above form of kinetic curve can easily be explained on the assumption of a first- or second-order reaction whose rate constant k has a wide distribution ($k_{max}/k_{min} \gg 1$), and that the reactants are initially uniformly distributed with respect to the non-equivalence parameter s, which is exponentially related to the rate constant and varies from zero to some value S:

$$k = k_{max}\, e^{-s} \quad (0 \leqslant s \leqslant S). \tag{9}$$

The kinetics of the variation in the macroscopic concentration of the initial substance A under these conditions is governed by an equation analogous to (6):

$$-\frac{d[A]}{dt} = \frac{1}{S}\int_0^S k_{max}\, e^{-s} A^n(s)\, ds, \tag{10}$$

where $1/S$ is a normalising factor, and n the order of the primary reaction, while the density of distribution $A(s)$ changes with time in conformity with the equation

$$-\frac{dA(s)}{dt} = k_{max}\, e^{-s} A^n(s) \tag{11}$$

If n is not too large and the initial distribution is uniform ($A(s) = [A]_0/S$ at $t = 0$), Eqns. (10) and (11) can be solved[15] quite accurately in the form

$$[A] \simeq -\frac{[A]_0}{S}[\ln(k_{max}[A]_0^{n-1}) - S + \ln t] \tag{12}$$

with $1 < k_{max}[A]_0^{n-1} t < e^S$. For $n = 1$ the more exact solution

$$[A] = -\frac{[A]_0}{S}[\ln(1.76 k_{max}) - S + \ln t] \tag{13}$$

was obtained[16].

The specific experimental procedure, i.e. kinetic study of the loss of active centres at different temperatures, made it natural to assume that kinetic non-equivalence of species was due to different heights of the energy barrier opposing chemical reaction. This corresponded formally to a distribution of rate constants according to activation energies:

$$S = \frac{E_{max} - E_{min}}{RT}. \tag{14}$$

However, no evidence was found to support this hypothesis. Similarly, for a long time only kinetic evidence was available for the view that the peculiar kinetics of such chemical processes in a solid phase might be due to kinetic non-equivalence of species in a macroscopically homogeneous medium.

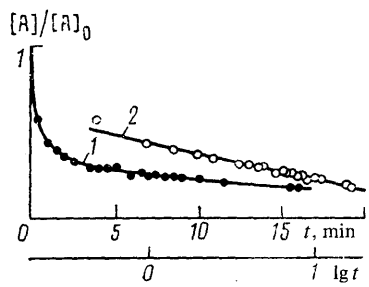


Figure 2. Destruction at 116 K of radical-pairs formed by the low-temperature (77 K) photolysis (300–400 nm) of frozen solutions of tetraphenylhydrazine in toluene: 1) kinetic curve; 2) semi-logarithmic transform (Eqn.12).

Direct evidence for such views was obtained only when effectively unimolecular processes, uncomplicated by a mechanism of approach of reactant species, began to be examined in terms of kinetic non-equivalence, and also when it became possible to halt a chemical reaction by different methods, and during the period of arrest to change the reactivity distribution of species without any change in the chemical composition of the system. The change in the effective rate of the process after such interruption served both as evidence of the validity of the model of kinetic non-equivalence of species and as a measure of the change in their reactivity distribution.

The first effectively unimolecular process examined from this point of view was the destruction of radical-pairs[15]. Electron spin resonance showed that pairs of radicals 3–6 Å apart can be generated in solutions of certain organic compounds. For example, pairs with

the radicals 4 ± 0.2 Å apart have been recorded in a solution of tetraphenylhydrazine in toluene. The destruction of such radical-pairs obeys "stepwise" kinetics corresponding to Eqn. (13).

Fig. 2 shows an example of a kinetic curve for the destruction of radical-pairs and its transform plotted in the variables of Eqn. (12). These results can be explained on the assumption that the width of the distribution of the rate constants exceeds a thousandfold. Accepting in conformity with formula (9) a rectangular distribution with respect to s for the species whose decay is plotted in Fig. 2, we find that $S = 10$. It was suggested[15] that the distribution of rate constants was due solely to the distribution of activation energies and found that $\delta E = 2.3 \pm 1$ kcal mole^{-1}. Because of the narrow temperature range (100–120 K) in which the kinetics of pair destruction could conveniently be recorded, it could not be established whether the distribution of rate constants was determined by the activation energy or the pre-exponential factor. Nevertheless, since the distance between the radicals in a pair is small and almost the same for all pairs, the observed kinetics cannot be explained by peculiarities in the mutual approach of radicals. In fact a pseudounimolecular reaction takes place, whose efficiency can be influenced only by the local environment of the reacting species. It was thus shown[15] that chemical reactions could actually occur under conditions of kinetic non-equivalence of the reactant species when the time during which the local properties of the medium remain constant exceeds significantly the other characteristic times of the process.

However, kinetic non-equivalence of reactant species could be observed especially clearly in photochemical reactions, the first example being the photo-oxidation of fused-ring hydrocarbons (anthracene, naphthacene, rubrene)[16,17]. This reaction involves singlet oxygen formed on interaction between a hydrocarbon molecule in a triplet state and a molecule of ordinary triplet oxygen. The product—a transannular peroxide—can be formed by reaction of singlet oxygen either with the same hydrocarbon molecule or with another, to which it diffuses through the medium. Singlet oxygen is a relatively small molecule, probably differing little in mobility from an ordinary oxygen molecule. Therefore the character of the diffusion of this active species in any medium is known, and in quantitative descriptions use can quite confidently be made of data on diffusion coefficients of diatomic gases, which have been measured in many media.

The kinetic scheme of the photo-oxidation of a fused-ring hydrocarbon can be written

$$\begin{aligned} &A + h\nu \rightarrow A^* \rightarrow A^T, \\ &A^T + {}^3O_2 \xrightarrow{k_0} A + {}^1O_2, \\ &A^T + {}^3O_2 \xrightarrow{k_{r0}} AO_2, \\ &A + {}^1O_2 \xrightarrow{k_r} AO_2, \\ &Q + {}^1O_2 \xrightarrow{k_q} {}^3O_2, \\ &{}^1O_2 \xrightarrow{k_d} {}^3O_2, \end{aligned} \qquad (15)$$

where A, A*, and A^T are molecules of the oxidisable compound in ground, excited, and triplet states, $^3O_2$ and $^1O_2$ are oxygen molecules in the triplet ground and the singlet states, Q is the quenching agent, and AO_2 is the transannular peroxide; the symbols above the arrows denote the corresponding rate constants.

According to the law of mass action, under quasi-stationary conditions with respect to singlet oxygen, the rate of change of the concentration of the oxidisable compound should be given by the equation

$$\frac{d[A]}{dt} = \alpha\left[1 - \gamma\left(1 - \frac{(k_r/k_d)\cdot[A]}{1 + (k_r/k_d\cdot[A] + (k_q/k_d)[Q]}\right)\right][A], \qquad (16)$$

where α is the product of the probability of absorption of a light quantum by an oxidisable molecule in unit time and the quantum efficiency η of formation of singlet oxygen, while $\gamma = k_0/(k_0 + k_{r0})$ is the probability of the escape of singlet oxygen into space.

However, Eqn. (16) describes the kinetics right up to high degrees of conversion only when photo-oxidation takes place in a sufficiently fluid medium. In solid polymers at temperature considerably below the glass point it describes satisfactorily only the initial stage: at later stages the process slows down significantly more rapidly than is required by Eqn. (16). Yet no data have been obtained on the occurrence in the system of any primary steps other than those listed in scheme (15). The kinetics of the variation in the concentration of the oxidisable compound is determined solely by the quantity of light incident on the specimen, independent of its intensity. This indicates that no two-quantum processes occur, interaction between intermediate species is absent, and a sufficient quantity of oxygen diffuses into the specimen. Reactant concentrations can be recorded during the process both from the variation in the absorption spectra and from the change in intensity of fluorescence of the initial substance. Hence no quenching agents are formed during the process.

The observed kinetics was explained on the hypothesis of a non-equivalent environment of the oxidisable molecules. Because of the relative immobility of the polymer matrix the relative proportion of molecules in an environment favourable for oxidation diminishes during the process, and hence also the effective overall quantum efficiency. This hypothesis has been confirmed by direct experiment[17,18]. It was found that photo-oxidation takes place significantly more efficiently if the process is periodically interrupted and the specimen is heated in the dark to temperatures close to the glass point. This affects neither the concentration of the oxidisable substance, its absorption and fluorescence spectra, nor the quantum efficiency of fluorescence. However, after such thermal activation the process conforms to Eqn. (16) until high degrees of conversion are reached, provided that the thermal activation is conducted at a sufficiently high temperature for a sufficiently long time, sufficiently frequently, and after equal periods of illumination.

Such a result was obtained in various polymer matrices with thermal activation at ~20 deg below the glass point for 10–20 min. In polypropylene and BMK-5 (a copolymer of methacrylic acid and butyl methacrylate having $T_{gl} = 40^\circ$C) at room temperature the process satisfies Eqn. (16), and is uninfluenced by thermal activation. The explanation for these results is that the thermal activation increases the mobility of the polymer matrix, permitting restoration of the original reactivity distribution of the reactants. In polypropylene and BMK-5 the initial distribution remains unchanged throughout the process because the molecular mobility of the matrix is adequate at temperatures close to or above the glass point.

For a quantitative description of the results a model was proposed in which the kinetic non-equivalence of the oxidisable molecules was attributed to differences in

permeability to singlet oxygen of the surrounding cage walls. Permeability can be characterised by the parameter u_0 occurring as a factor in the primary formation and decomposition rate constants k_1 and k_2 of the "singlet oxygen–oxidisable substance" pair. Provided that spontaneous breakdown of $^1O_2$ molecules in the cage can be neglected, k_r and γ will then be given by the formulae

$$k_r = \frac{k_1 k_3 u_0}{k_2 u_0 + k_3}, \tag{17}$$

$$\gamma = \frac{k_2 u_0}{k_2 u_0 + k_3}, \tag{18}$$

where k_3 is the oxidation rate constant in the pair.

The parameter u_0 has different values for different molecules of the oxidisable substance, but remains unchanged throughout the process in the absence of thermal activation. On such a model the form of the kinetic curve for consumption of the oxidisable compound is determined not only by the magnitude of the kinetic parameters but also by the kinetics of the change in the distribution function $\rho(u_0)$ of oxidisable molecules among cages differing in permeability. Assuming that the initial form of distribution is independent of the macroscopic concentration of the oxidisable compound, while the local concentration of singlet oxygen corresponds to its average concentration in the specimen, we obtain for the kinetics of variation in the concentration of the oxidisable substance, instead of (16), the equation

$$\frac{d[A]}{dt} = -(\alpha I_1 + k_1 I_2 [^1O_2]) k_3 [A], \tag{19}$$

in which

$$I_1 = \int \frac{\rho(u_0)\, du_0}{k_2 u_0 + k_3}; \quad I_2 = \int \frac{u\rho(u_0)\, du_0}{k_2 u_0 + k_3}.$$

The distribution $\rho(u_0)$ is normalised only at zero time: $\rho(u_0)du_0 = 1$ at $t = 0$.

If the concentration of singlet oxygen $^1O_2$ is quasi-stationary, we find that

$$[^1O_2] = \frac{\alpha k_2 I_2 [A]_0}{k_1 k_3 I_2 [A]_0 + k_d}. \tag{20}$$

Substitution of (20) in (19) yields the equation

$$\frac{d([A]/[A]_0)}{dt} = -\alpha k_3 I_1 - \frac{\alpha k_1 k_2 k_3 I_2^2 [A]_0}{k_1 k_3 I_2 [A]_0 + k_d} \tag{21}$$

which describes the variation in concentration of the oxidisable substance right until high degrees of conversion are reached.

We can make a similar approach to the more general case, taking into account the quenching of $^1O_2$ molecules in the pair with rate constants k'_d and a possible difference in probability of chemical interaction in pairs formed after absorption of a light quantum and in those formed after an encounter between $^1O_2$ and an oxidisable molecule. With rate constants and parameters corresponding to pairs of the former type primed, the appropriate equation is

$$\frac{d([A]/[A]_0)}{dt} = -\alpha \left(k'_3 I'_1 + \frac{k_1 k'_2 k_3 I'^2_2 [A]_0}{k_1 (k_3 + k'_d) I_2 [A]_0 + k_d} \right), \tag{22}$$

in which

$$I'_i = \int \frac{u_0^{i-1} \rho(u_0)\, du_0}{k_3 + k'_d + k_2 u_0}.$$

The time dependence of the distribution $\rho(u_0)$ normalised at zero time conforms to an equation analogous to (19):

$$\frac{d\rho(u_0)}{dt} = -\alpha \frac{k_3}{k_2 u_0 + k_3} \left(1 + \frac{k_1 k_2 u_0 I_2 [A]_0}{k_1 k_3 I_2 [A]_0 + k_d} \right). \tag{23}$$

The complexity of the solution of (23) is due to the variation of the integral I_2 with time. At low concentrations of the oxidisable substance terms containing I_2 can be neglected, and (23) can be solved similarly to (11). Assuming that the probability of chemical interaction in a pair is related exponentially to some parameter s_0 distributed uniformly between 0 and S_0‡

$$\frac{k_3}{k_2 u_0 + k_3} = e^{-s_0}, \tag{24}$$

we obtain instead of (23) the equation

$$\frac{d\rho(s_0)}{dt} = \frac{1}{S_0} \alpha e^{s_0} \rho(s_0) \tag{25}$$

which is analogous to (11).

If we neglect also diffusion of oxidisable molecules through cages having different values of s_0, the kinetics of the variation in the concentration of the oxidisable compound will be described by an equation analogous to (13):

$$[A] = [A]_0 \left(1 - \frac{1}{S_0} \ln(1.76\alpha t) \right). \tag{26}$$

At high concentrations of A we find an approximate solution analogous to (12):

$$[A] = [A]_0 \left[1 - \frac{1}{S_0} \ln\left(Z_1 \alpha t \frac{Z_2}{1 + Z_2 - \alpha t} \right) \right], \tag{27}$$

where $Z_2 = k_d / k_1 k_3 I_2 [A]_0$ and Z_1 is a factor exceeding unity (but in the present case probably not exceeding 2) characterising the form of the $\rho(u_0)$ kinetic curve. The initial rate under these conditions is given by

$$\left(\frac{d([A]/[A]_0)}{dt} \right)_{t=0} = -\alpha Z_1 \left[\frac{1 - e^{-S_0}}{S_0} - Z_2 \left(1 + \frac{1 - e^{-S_0}}{S_0} \right) \right]. \tag{28}$$

With a sufficiently wide distribution Eqn. (28) can be simplified to

$$\left(\frac{d([A]/[A]_0)}{dt} \right)_{t=0} = -\alpha Z_1 \left(\frac{1}{S_0} - Z_2 \right). \tag{29}$$

In the study of the destruction of free radicals it is usually difficult to determine the initial rate, since the specimen heats up during the reaction, so that the initial stage takes place at a lower temperature than the process as a whole. Such difficulties do not arise with a photochemical process, which begins almost without inertia. Comparison of data on its initial rate with the kinetics of variation in concentration at later stages can therefore be used for quantitative verification of the above ideas[17,18].

Thus ideas on the kinetic non-equivalence of reactant species have provided a kinetic description of photo-oxidation, which is formally more complicated than the destruction of free radicals. However, photo-oxidation of hydrocarbons can be conducted under conditions such that the kinetics are simpler. At low concentrations of the oxidisable substance, when reactions of singlet oxygen that has escaped from the cage in which it had been formed

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‡If the ratio $k_2 u_0 / k_3 \gg 1$ for all u, the significance of S_0 is a quantity proportional to the free energy of activation of the chemical reaction: $S_0 = \Delta G/RT = \Delta S/R + E/RT$.

can be neglected, photo-oxidation takes place within a single cage: i.e. it is formally a unimolecular reaction, uncomplicated by transport of the reactant species to each other. Furthermore, it is a photoreaction, which can be arrested or restarted by switching the radiation off or on. This advantage has opened up new technical possibilities—of studying the kinetics of the variation in reactivity of a substance in the absence of chemical change.

IV. KINETICS OF VARIATION IN REACTIVITY

The first kinetic studies of the variation in the reactivity of molecules located in a solid matrix (Section III) showed[16,17] that the initial reactivity of fused-ring hydrocarbons towards photo-oxidation could be restored by heating the specimens to temperatures 10–30 deg below the glass point of the matrix for a few minutes. This provided estimates of the temperature and time scales required to restore the original reactivity distribution of the molecules.

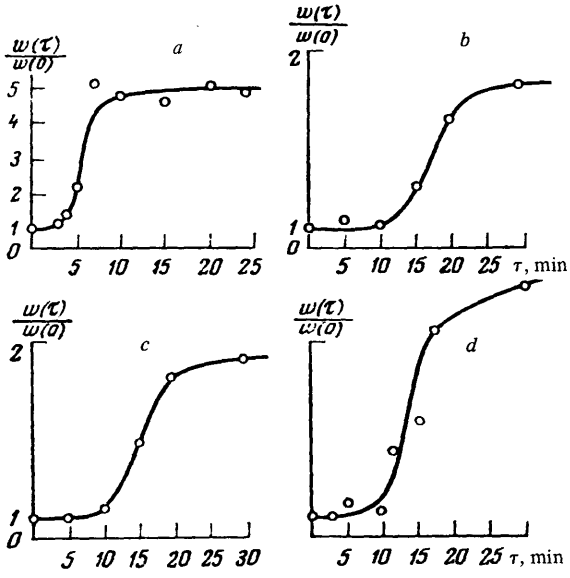


Figure 3. Dependence of relative rate of photo-oxidation $w(\tau)/w(0)$ on duration of thermal activation: *a*) 1.36 mM naphthacene in polystyrene (activated at 70°C, conversion 80%); *b*) 1.36 mM naphthacene in poly(methyl methacrylate) (52°C, 40%); *c*) 5.6 mM anthracene in polystyrene (70°C, 40%); *d*) 3.1 mM naphthacene in polystyrene (60°C, 60%).

In a more detailed study[19] fused-ring hydrocarbons were subjected in polymer films to photo-oxidation at 20°C until a specified degree of conversion was attained. The specimen was then heated in the dark at a fixed temperature T for a certain time τ. After this the specimen was again exposed at 20°C, and the rate of change in the concentration of the oxidisable substance during the second exposure was recorded. The variation in the rate of the process with different times of heating provided a measure of the variation in reactivity of the oxidisable compound during heating. Fig. 3 illustrates the dependence of the relative rate of the second photo-oxidation $W(\tau)/W(0)$ on the time of heating τ at different temperatures. As could have been expected, rise in the temperature of thermal activation accelerates restoration of the equilibrium rate of oxidation; the range of variation in the rate expands with increase in the initial degree of conversion.

A striking feature of Fig. 3 is the sigmoid form of the dependence of rate of photo-oxidation on time of thermal activation at sufficiently high degrees of primary conversion. From simple considerations it might have been expected that maximum rate of change of reactivity would occur with short times of thermal activation, when the reactivity distribution of the species would be most remote from equilibrium. This might have occurred if the change in reactivity had resulted from movement of fluctuations of the free volume through a macroscopically homogeneous specimen[12]. On such a model any molecule can change its reactivity abruptly on thermal activation, passing into a state corresponding to equilibrium. The probability of such a jump is independent of the state of the molecules before thermal activation.

On the other hand, a sigmoid dependence can be observed only if the initial reactivity of the molecule has a significant influence either on the sequence of states through which it passes during thermal activation or on the probability of a change in reactivity. This type of dependence may be expected, for example, if thermal activation involves continuous "diffusion" of molecules from a non-equilibrium to an equilibrium reactivity distribution. We postulate that molecular reactivity χ is determined by a parameter u_1 characterising the state of the molecule in the given medium. Under equilibrium conditions there exists a certain distribution of species according to this parameter $\rho_0(u_1)$. During the first photo-oxidation, when thermal diffusion among states can be neglected, the equilibrium distribution is disturbed by occurrence of the chemical reaction, so that

$$\rho(u_1, t) = \rho_0(u_1)\exp(-\chi(u_1)t), \tag{30}$$

where t is the time of photo-oxidation.

During thermal activation continuous diffusion through states differing in u_1 value will be described by the equation

$$\frac{\partial\rho}{\partial\tau} = D\frac{\partial^2\rho}{\partial u_1^2}, \tag{31}$$

where τ is the time of thermal activation and D the corresponding diffusion coefficient. The boundary conditions for Eqn. (31) correspond to absence of diffusion beyond the extreme values of u_1:

$$\left.\frac{\partial\rho}{\partial u_1}\right|_{u_{1\,\min},\tau} = \left.\frac{\partial\rho}{\partial u_1}\right|_{u_{1\,\max},\tau} = 0. \tag{32}$$

With certain forms of the distribution $\rho_0(u_1)$ the solution of Eqn. (31) enables a sigmoid dependence to be obtained. This occurs, for example, with D constant and independent of u_1, i.e. with the uniform distribution $\rho_0(u_1)$ = const, when

$$\chi(u_1) = -k_0\ln\left(\sin\frac{u_1}{2}\right); \quad 0 \leqslant u_1 \leqslant \pi, \tag{33}$$

and at degrees of conversion during the first photo-oxidation exceeding 50%.

The above results do not give the reasons for the non-equivalence of reactant species. However, they must be taken into account in constructing models to explain this phenomenon.

V. KINETICS WITH PARTIAL KINETIC NON-EQUIVALENCE OF REACTANT SPECIES

As noted above, under conditions such that the correlation time τ_c of reactant species over all possible states in the medium is intermediate between the time τ_x of significant change in concentration of the reactant species and the lifetime of an active centre τ_e, i.e. when

$$\tau_x \gg \tau_c \gg \tau_e, \tag{34}$$

the variation in macroscopic concentration obeys the usual kinetic laws, while kinetic non-equivalence of the species merely disturbs classical ideas on the relative rates of different possible reactions.

Conditions for such partial kinetic non-equivalence of reactant species can be realised especially easily in photochemical processes. If the light is not too intense, such a process comprises a series of consecutive or parallel physical or chemical changes lasting a relatively short time after absorption of a quantum (usually $\tau_e \ll 1$ s). Each such process usually proceeds until a certain stage is reached, independently of the occurrence of other primary processes initiated by the absorption of other light quanta. Therefore the time τ_e for development of a primary photochemical process is independent of the light intensity. Yet τ_x does depend on the intensity, and usually exceeds τ_e considerably, amounting to minutes, hours, or longer. Evidently, therefore, it is not difficult to find a medium and a photochemical process for which the condition (34) of partial kinetic non-equivalence of reactant species will be satisfied.

A photochemical process can be influenced relatively easily by the introduction of additives that quench excited states. Under conditions of partial kinetic non-equivalence of excited species the intensity of luminescence and the rate of the photochemical process will then vary in different ways.

As example we can consider results for so called unstoppable photochemical processes, which cannot be completely inhibited when the luminescence of the leading species has been extinguished[20]. Phenomena of this type have been known for some time[21,22]. The most common class of photochemical processes involves species in the triplet state, and cannot be completely inhibited by the introduction of quenchers for such states. This is usually explained by the involvement of single excited molecules[23], but this hypothesis is fairly difficult to substantiate. Therefore an alternative explanation of unstoppable processes, based on the kinetic non-equivalence of reactant species, seems quite permissible.

The quenching of excited states by any mechanism can be described approximately by the Stern–Volmer equation[24]: the concentration of molecules in an excited state S^* is

$$[S^*] = \frac{w}{k_d + k_f + k_r + k_q[Q]}, \tag{35}$$

where w is the rate of formation of excited molecules, k_d and k_f are the rate constants of spontaneous and radiative deactivation of excited molecules, k_r is the rate constant of their chemical reaction in the given medium, and k_q is the rate constant of the quenching of S^* by a quencher molecule Q. If, however, the excited molecules are kinetically non-equivalent, Eqn. (35) represents the effect of the quenching agent on the concentration of only one species. Then the total macroscopic concentration of excited species will be described by the integral over all possible local properties that can be effective in the given medium:

$$[S^*] = \int \frac{w\rho(u)\,du}{k_d + k_f + k_r + k_q[Q]}, \tag{36}$$

where u is a parameter representing these properties and $\rho(u)$ the density of distribution of concentration with respect to this parameter. In general all the other quantities in (36) are also functions of u.

The quantum efficiencies of luminescence η and of the photochemical process φ will be given by analogous formulae:

$$\eta = \alpha' \int \frac{k_f \rho(u)\,du}{k_d + k_f + k_r + k_q[Q]} \tag{37}$$

$$\varphi = \alpha' \int \frac{k_r \rho(u)\,du}{k_d + k_f + k_r + k_q[Q]} \tag{38}$$

From these expressions we find that quenchers of excited states have different effects on the intensity of luminescence and on the rate of the photochemical process:

$$\frac{\varphi}{\varphi_0} \neq \frac{\eta}{\eta_0}.$$

Equations (37) and (38) have been subjected[25] to detailed analysis for the case in which the kinetic non-equivalence of the excited molecules is due to the effect of the local properties of the medium on k_r. The character of the $\rho(u)$ distribution is examined by comparing the efficiency of the quenching of luminescence and of the inhibition of the photochemical process by small additions of the quenching agent

$$Z = \left(\frac{\partial(\eta/\eta_0)}{\partial[Q]}\right)_{[Q]=0} \Big/ \left(\frac{\partial(\varphi/\varphi_0)}{\partial[Q]}\right)_{[Q]=0} \tag{39}$$

with the type of deviations from the Stern–Volmer equation of the variation of the quantum efficiencies η and φ with the quencher concentration. It was shown that only one of the variations in quantum efficiency—either of the photochemical process or of luminescence—can be expected to diverge considerably from the equation. Quenching agents are always more effective in quenching luminescence than in inhibiting a photochemical process ($Z \leq 1$). If a uniform distribution is assumed for the entropy factor S of the chemical reaction rate constant, as is done by many authors in discussing processes with complete kinetic non-equivalence of species (9), considerable deviations from the Stern–Volmer equation appear to be possible only at sufficiently small ratios Z. To explain such departures when Z is large we must postulate other types of distribution, in particular bimodal, based on the presence of two kinds of local conditions, under which excited molecules have significantly different reactivities.

This last hypothesis has been used[28] to explain the effect of oxygen on the photodecomposition and the phosphorescence of benzophenone in poly(methyl methacrylate). Plots of the quantum efficiencies show (Fig. 4) that oxygen is almost twice as effective in quenching phosphorescence as in retarding photodecomposition ($Z \simeq 0.6$), and the Stern–Volmer equation does not describe the inhibition of the photochemical process. These results can be understood on the hypothesis that $\rho(u)$ is bimodal: the lifetimes of triplet benzophenone molecules corresponding to different local conditions differ more than fourfold; and the

probability of chemical reaction for species possessing shorter lifetimes exceeds 0.75, while the probability of formation of such species is ~0.4.

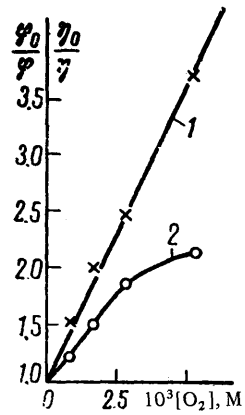


Figure 4. Effect of oxygen on quantum efficiency in 0.29 M benzophenone in poly(methyl methacrylate) exposed to light of wavelength 365 nm and intensity 10^{17} cm^{-2} s^{-1}: 1) phosphorescence; 2) photochemical conversion.

VI. INFLUENCE OF MOBILITY OF MEDIUM ON EFFICIENCY OF PRIMARY CHEMICAL REACTIONS

On passing from liquid-phase systems to solid solutions we find not only the above kinetic features of solid-phase reactions but also a qualitative change in the relative reactivities of species differing in chemical structure. In viscous solutions, especially media that can be regarded as solid, when effective chemical reaction rate constants are remote from diffusion constants, i.e. when encounter between reactant species cannot be the rate-determining stage, a considerable levelling is observed in the activities of chemically different species.

A method for measuring the relative efficiencies with which inhibitors differing in structure act on peroxy-radicals in a solid polymer matrix is based[26,27] on a study of the influence of the inhibitors on the initial rate of consumption of stable quinoline or di-*p*-methoxyphenyl-nitroxide radicals (R_{quin}· or R_{dmpn}·) during initiated oxidation of the polymer. Table 1 shows that the rate constants for interaction of different valency-saturated inhibitors with peroxy-radicals are almost the same in solid polystyrene, whereas they differ hundredfold in the liquid phase. The observed levelling of inhibitor activity cannot be explained by diffusion limiting reaction in the solid phase, with the limiting value of the constant representing the diffusion mobility of the reactants. Such a suggestion is contradicted by the fact that the activity of stable radicals exceeds by factors of 10–20 the "limiting" activity of valency-saturated inhibitors. Since there are no data indicating an abnormally high diffusion coefficient for stable radicals, the result suggests that the levelling effect is not merely a restriction on translational mobility, but has a more complex nature and probably depends on the type of reaction.

Table 1. Effect of polymer matrix on antiradical activity of antioxidants at 70°C.

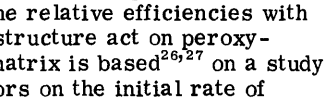
Antioxidant	$10^{-4}k_7$, M^{-1} s^{-1}	
	ethylbenzene	polystyrene*
stable radicals		
R_{quin}·	124	51
R_{dmpn}·	46	30
valency-saturated inhibitors		
1-Naphthol	44	3.6
Bis-(3-t-butyl-5-methylphenyl)methane-2,2'-diol	41	5.1
Tin thio-2,2'-bis-(4-methyl-6-α-methylbenzyl-phenol)	20	4.2
Calcium oxide-bis-(3-t-butyl-2-hydroxy-5-methylphenyl)sulphide	18	3.6
Phenylnaphthylamine	13	2.2
Pentaerythritol β-(3,5-di-t-butyl-4-hydroxy-phenyl)propionate	4.7	1.9
Bis-(3,5-di-t-butylphenyl)methane-4,4'-diol	2.6	1.5
2,6-Di-t-butyl-4-methylphenol	2.5	2.8
Phenol	0.3	0.3

* Absolute values of the constants determined on the assumption that k_7 for phenol is the same in polystyrene as in ethylbenzene.

Table 2. Change in efficiency of reaction of $^1O_2$ with various compounds on passing from the liquid phase to a solid polymer.

Compound	Efficiency of chemical action $10^{-3}k_r/k_d$, M^{-1}		Efficiency of quenching $10^{-3}k_q/k_d$, M^{-1}		
	CH_2Cl_2	polystyrene	CH_2Cl_2	BMK-5*	polystyrene
β-Carotene	15	0.12	3600	—	8
Nickel dibutyldithiocarbamate	—	—	470	1.3	1.1
Rubrene	9	0.14	—	—	—
Di-*p*-methoxyphenylamine	—	—	9.1	0.5	—
1,2,2,6,6-Pentamethylpiperidine	—	—	7.3	—	0.42
Naphthacene	2.5	0.08	—	—	—
2,4-Xylidine	—	—	3.2	0.2	—
1-Naphthylamine	—	—	2	0.22	—
Bismuth dimethyldithiocarbamate	—	—	1.5	—	0.24
Irgostab 2002**	—	—	0.51	0.19	0.17
Di-*p*-iso-octylphenylamine	—	—	0.12	0.072	—
N-n-Butylphenylnaphth-2-ylamine	—	—	0.041	0.038	—
Anthracene	0.018	0.0037	—	—	—

* A copolymer of methacrylic acid and butyl methacrylate.

**  Ni with R = t-C_4H_9.

A similar effect has been found for the rate constants in the quenching of singlet oxygen by various substances and its reaction with aromatic hydrocarbons (Table 2).[28-30] Here the levelling is still more clearly defined: in the liquid phase the difference in relative quenching rate constants reaches 10^5, but in the solid it does not exceed factors of 200–300. Such parallel variation in rate constants on passing from the liquid to the solid phase occurs only with reactions of the same type: rate constants for different types of reactions vary differently. Thus the rate constant for reaction between molecular oxygen and

rubrene in the liquid phase exceeds those for the quenching of oxygen by almost all substances other than β-carotene and nickel dithiocarbamate, but in solid polystyrene it becomes smaller than those for the action of oxygen on any of the quenching agents investigated. Change in reactivity leading to the levelling effect takes place at temperatures above the glass point of the medium[29]. A study of the efficiency of inhibitors in the thermal oxidation of polyalkenes revealed a levelling phenomenon at temperatures of ~100°C, more than 100 deg above the glass point[31].

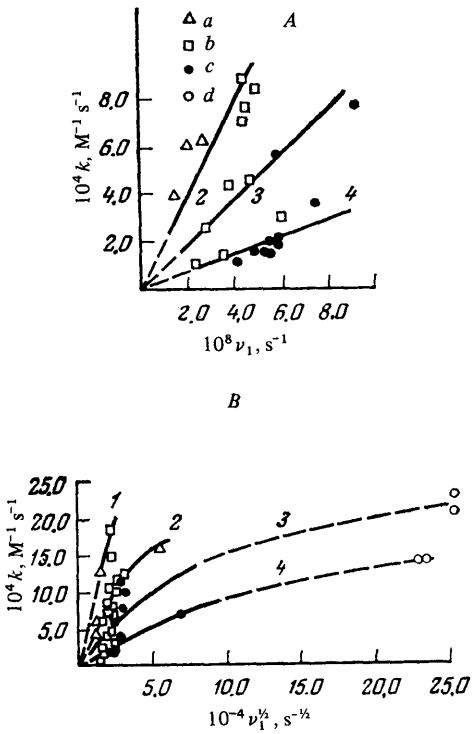


Figure 5. Dependence of rate constant k for reaction of >NO with phenol on frequency of rotation of paramagnetic probe: A) at low frequencies; B) over a wide frequency range in various media: *a*) polystyrene; *b*) polypropylene; *c*) polyethylene; *d*) benzene at different temperatures (°C): 1) 70; 2) 60; 3) 50; 4) 40.

Yet another phenomenon characteristic of reactions in a polymer matrix—the dependence of the reaction rate constant, not limited by diffusion, on the mobility of the medium—has been observed[32-36] in the same matrix at about the same temperature. The reaction of 2,4,6-tri-t-butylphenoxyl with hydroperoxy-groups in polyalkenes exhibits a correlation between its rate constant and the frequency of rotation of a stable nitroxyl radical in the same polymer matrix[32,34]. This correlation was interpreted as due to the effect of the cage on the probability and the rate of change of the mutual orientation of the species in the cage[35]. Rate constants for this reaction[32,34] and for that between the nitroxyl radical 4-benzoyloxy-2,2,6,6-tetramethylpiperidino-oxyl (>NO·) and 2,6-di-t-butylphenol[36] are determined by the change in the frequency of rotation of a paramagnetic probe, and are independent of the nature of the matrix in which the reaction occurs (Fig. 5). Hence the differences in activation energy of these reactions in different media are governed by the difference in the activation energy of rotational mobility in them.



Figure 6. Influence of mobility of medium on ratio of times of translational and rotational diffusion ($n = \tau_{rot}/\tau_{tr}$, with $\tau_{tr} = x/2D_{tr}$ (x = 5 Å) and $\tau_{rot} = 1/6D_{rot}$, where x is the translational displacement of the probe, and D_{tr} and D_{rot} are the coefficients of translational and rotational diffusion) in rubbers at different temperatures: 1) polyenes; 2) polybutyl rubbers.

Both phenomena—levelling of the activity of structurally different species involved in reactions of the same class and the effect of the mobility of the medium on reactions not limited by diffusion—probably have the same origin, change in character of the motion of the species on passing from a liquid to a solid medium. Evidence in support of this suggestion is provided by the fact that the ratio of the correlation time of a paramagnetic probe to the characteristic time of its translational mobility increases with the viscosity of the medium (Fig. 6).[37] Increase in viscosity is probably accompanied by an increase in the number of rotations by the molecule relative to the walls before it escapes from the cage. This tends to increase the probability of chemical reaction when the reactant molecules meet. On passing to more viscous media, therefore, we must evidently expect not only a diminished probability of chemical reaction between species due to the diminished mobility of the medium, and hence also a lower probability that particles will meet, but also an increased probability of chemical reaction resulting from the longer lifetime of reactant species in the same cage.

To examine this last suggestion in greater detail we postulate that two molecules A and B meet, assuming for simplicity that B is considerably smaller than A and that

their relative motion can be represented as the movement of a point (B) over the surface of a sphere (A). When the point B enters some reactive region of area s on the spherical surface of A, reaction takes place without energy of activation. In the liquid phase the probability of reaction on the collision of A and B will be given by the ratio of s to the whole spherical surface area S_0, so that the rate constant of this reaction k_{liq} is related to the encounter rate constant $(k_D)_{liq}$ by the equation

$$k_{liq} = (k_D)_{liq} \frac{s}{S_0}. \quad (40)$$

In the solid phase the probability of reaction in an encounter P_{sd} is increased by movement of the point on the spherical surface during the lifetime of the pair. If $s \ll S_0$ and the path L traversed by the point on the surface is not too long, this probability will be given by the formula

$$P_{sd} = \frac{s}{S_0} + \frac{L}{\chi\sqrt{s}} \cdot \frac{s}{S_0}, \quad (41)$$

in which χ is a coefficient around unity, whose value depends on the configuration of the reactive region.

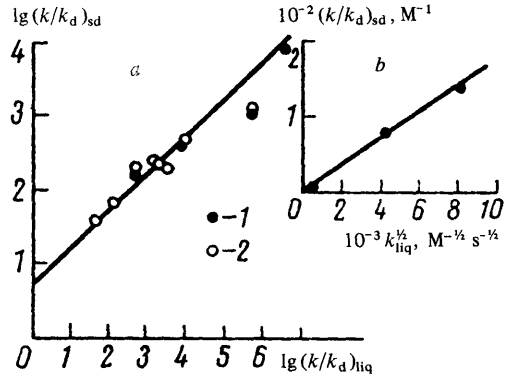


Figure 7. Comparison of rate constants for processes occurring in liquid and solid phases (k_{liq} in methylene dichloride and k_{sd} in: 1) polystyrene; 2) BMK-5: *a*) quenching of singlet oxygen; *b*) chemical interaction with $^1O_2$.

From Eqn. (40) it is easy to obtain a relation between the rate constants of the same reaction in liquid and solid phases:

$$\left(\frac{k}{k_D}\right)_{sd} = \left(\frac{k}{k_D}\right)_{liq} + \frac{L}{\chi\sqrt{S_0}}\left(\frac{k}{k_D}\right)_{liq}^{1/2}. \quad (42)$$

Since all the arguments have been conducted for a case in which the reaction rate constant is far from diffusion-controlled, the formula simplifies to

$$\left(\frac{k}{k_D}\right)_{sd} = \varphi\left(\frac{k}{k_D}\right)_{liq}^{1/2}, \text{where } \varphi = \frac{L}{\chi\sqrt{S_0}}, \quad (43)$$

i.e. the reaction rate constant in the solid phase is proportional to the square root of the rate constant of the corresponding liquid-phase reaction. Fig. 7*a* shows that Eqn.(43) describes satisfactorily the results[30] in Table 2 on the quenching of singlet oxygen by various agents: the formula is satisfied for a variation in the reactivity of quenching agents in the liquid phase by factors $>10^5$.

The above reasoning is consistent also with the reactivities of valency-saturated inhibitors and stable radicals towards peroxy-radicals[26,27] (Fig. 8) and with data on the chemical interaction of singlet oxygen with fused rings[28,29] (Fig. 7*b*).

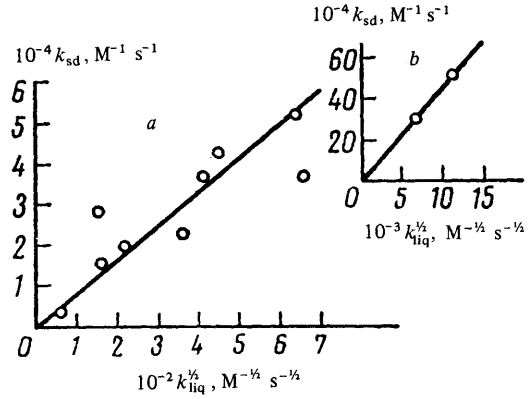


Figure 8. Comparison of rate constants in liquid and solid phases (k_{liq} in ethylbenzene and k_{sd} in polystyrene) for interaction of peroxy-radicals with: *a*) valency-saturated inhibitors; *b*) stable radicals.

The parameter φ has been estimated[30] from the deactivation rate constant k_d and the diffusion coefficient of singlet oxygen. The active centre traverses on the surface of the larger molecule a path of the order of the length of a great circle. This result tends to validate the approximation of a relatively short path made in deducing formula (41).

The models discussed above are evidently extremely rough approximations. However, the experimental results can be explained on the hypothesis that steric factors of the rate constants of chemical reactions in liquid and solid phases are interrelated by the above formulae. The essence of the models is that variation in reactivity is determined by significant change in character of the motion of the reactant species. In the liquid phase this merely involves the meeting or collision of two species; but in the solid phase comparatively lengthy relative motion in the pair is involved.

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It has been thus been shown above that the main kinetic features of solid-phase reactions can be explained in terms of the single concept of a difference between solid and liquid phases in the character of the motion of reactant species in them. Transition from an ideal liquid to an ideal solid involves a sequence of qualitative changes in chemical kinetics. In a relatively mobile medium (at temperatures above the glass point) the relation between the reactivity of chemically different species changes,

and their activities level off within a given class of reactions. Roughly under the same conditions the mobility of the medium begins to influence significantly the rate constants of the primary reactions. In more rigid matrices (below the glass point) the relative immobility of the medium does not allow "mixing" of relative species among all possible states in the given medium, which entails the appearance of unusual chemical kinetics.

Several aspects of practical importance—the causes of kinetic non-equivalence of species in structurally different cages, the nature of the relation between the kinetics of variation in cage structure and the kinetics of molecular motions of the matrix, the properties of the medium governing the influence of the motion of species in a cage on their reactivity—remain open questions. The last problem is especially important, since there are indications[36] that a transition from "liquid-phase" to "solid-phase" reactivity occurs in polyalkenes at temperatures above 100°C, more than 100 deg above the glass point, and thus under conditions such that the medium can no longer be regarded as a solid but as a very viscous liquid. It is therefore possible that certain kinetic features of solid-phase reactions can be observed even in ordinary liquid-phase processes.

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Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow