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Testing of Chemical Compounds as Stabilisers for Polymeric Materials

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Test methods are briefly surveyed, a scheme of testing is examined, and experimental results obtained by means of the scheme are discussed. A list of 69 references is included.

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I. INTRODUCTION

Most cases of the degradation of polymeric materials involve a free-radical chain mechanism; this enables the rate of degradation to be lowered substantially by introducing into the polymer a small quantity of a special substance to act as a stabiliser. The latter often functions either by deactivating the active radicals in the chain process or by decomposing intermediate products that provide a source of active radicals. In view of the continuous growth in the manufacture of various polymeric materials and substances for their stabilisation, the testing of chemical compounds as stabilisers has become an urgent problem.

On the basis of achievements of current research on the kinetics and the mechanism of chain processes a team including the Reviewers, headed by Academician N. M. Emanuel'[1-3] at the Institute of Chemical Physics of the USSR Academy of Sciences, has developed during recent years a set of methods for the rapid and reliable quantitative assessment of various chemical compounds as potential stabilisers for polymers whose degradation takes place by a free-radical chain mechanism. The scheme includes methods for preliminary assessment of effectiveness on model reactions (screening) and methods for the accelerated testing of compounds in polymers and polymeric materials.

II. PRELIMINARY ASSESSMENT BY MEANS OF MODEL REACTIONS

The testing of a chemical compound begins with a quantitative assessment of its chemical reactivity on model systems. Thus oxidative degradation is simulated by chain oxidation of simple compounds, whose mechanism has now been studied quite thoroughly[4-8]. The applicability of such reactions as models has a theoretical basis in the common mechanism of oxidation of organic compounds having low and high molecular weights[9-11]. In particular, peroxy-radicals function as active centres in these chain processes. The active centres in the thermal degradation of polymers are often alkyl radicals. Chain polymerisations, whose mechanism has also been thoroughly studied[12-19], are therefore used as models of thermal degradation.

The effectiveness of a chemical compound as a potential stabiliser is determined by its ability to slow down initiated chain oxidations[20,21] and polymerisations[21-23]. Various kinetic parameters, characterising such retardation, can be used as criteria of efficiency. Examples are the ratio of the rates of reaction in the absence and in the presence of the test compound, the decrease in the extent of the process (yield of polymer), etc.

Initiated oxidations and radical polymerisations can be represented by the simple scheme

$$\text{(A) Chain initiation; } W_i - \text{ rate of initiation ,} \tag{1}$$

$$\text{(B) Chain propagation: } R_1H + n_1 \xrightarrow{k_{p11}} n_1 + \text{ Product ,} \tag{2}$$

$$\text{(C) Chain termination: } 2n_1 \xrightarrow{k_{t11}} \text{ Inactive products ,} \tag{3}$$

where R_1H is the hydrocarbon or the monomer, n_1 is an active centre, and k_{p11} and k_{t11} are the rate constants of chain propagation and termination respectively. For sufficiently long chains the rate of the process is given by the equation

$$W = W_i^{1/2} \frac{k_{p11}}{k_{t11}^{1/2}} [R_1H]. \tag{4}$$

A more general scheme for a chain process in the presence of a substance R_2H (which may be a stabiliser) can be written

$$\text{(A) Chain initiation; } W_i - \text{ rate of initiation ,}$$

$$\text{(B) Chain propagation: } \begin{cases} R_1H + n_1 \xrightarrow{k_{p11}} n_1 + \text{ Product ,} \\ R_1H + n_2 \xrightarrow{k_{p12}} n_1 + \text{ Product ,} \\ R_2H + n_1 \xrightarrow{k_{p21}} n_2 + \text{ Product ,} \\ R_2H + n_2 \xrightarrow{k_{p22}} n_2 + \text{ Product ,} \end{cases}$$

$$\text{(C) Chain termination: } \left.\begin{array}{ll} 2n_1 & \xrightarrow{k_{t11}} \\ n_1 + n_2 & \xrightarrow{k_{t12}} \\ 2n_2 & \xrightarrow{k_{t22}} \end{array}\right\} \text{ Inactive products .} \quad \begin{matrix} (5) \\ (6) \\ (7) \end{matrix}$$

The rates of the chain conversion of each substance and the overall rate of the process are described by the well known formulae for rates of co-oxidation and copolymerisation. These rates depend on the concentrations of R_1H and R_2H and the rate constants of chain propagation and termination. At low concentrations of R_2H (stabiliser

concentrations usually amount to 0.1–2%) the chain process is slowed down provided that[24]

$$\frac{k_{t12}}{k_{t11}} \cdot \frac{k_{p21}}{k_{p12}} - 2\frac{k_{p21}}{k_{p11}} > 1 .$$

Thus retardation depends on the choice of model reactions (rate constants k_{p11} and k_{t11}) and also on the three primary reactions involving R_2H and the radical formed from it. The greatest retardation is produced by substances that react rapidly with active centres (high rate constant k_{p21}) and by those from which unreactive radicals are formed (low rate constant k_{p12}).

If the additive is an inhibitor, i.e. if the radicals formed from it are inactive, we have $k_{p12} = 0$, and retardation of the chain process becomes indefinitely large. An expression for the rate of consumption of R_1H in an inhibited chain process (with $k_{p12} = 0$ and $k_{p22} = 0$) can be obtained only by making certain assumptions about the chain-terminating reactions[25]. The simplest formula is obtained by neglecting reaction (5)—quadratic termination of active centres n_1 (all active centres react with the inhibitor):

$$W_{inh} = W_i \frac{k_{p11}}{k_{p21}} \cdot \frac{(R_1H)}{(R_2H)}, \qquad (8)$$

where the inhibition coefficient $f = 1-2$ depending on the relative rates of reactions (6) and (7)†. From Eqns. (4) and (8) we find that

$$\frac{W}{W_{inh}} = \frac{f k_{p21} \cdot (R_2H)}{k_{t11}^{1/2} \cdot W_i^{1/2}} \qquad (9)$$

Thus the effect of inhibitors on the chain process is determined by the rate constant k_{p21} for reaction between inhibitor and active centre. Formula (9) can be used in many cases to assess the chemical activity of test compounds (various derivatives of amines, phenols[26], and other compounds that inhibit chain processes usually serve as stabilisers).

The rate constant k_{p21} is usually denoted by k_7 in oxidations and by k_Z in polymerisations. The nature of the oxidisable substance (the radical R·) has a slight effect on k_7.[25,27,28] A correlation may therefore be reasonably expected between this constant k_7 and the stabilising effect of the test compound. Such a correlation has indeed been established for several phenols: the more readily the peroxy-radical of tetralin abstracts the hydrogen atom from the phenol (the higher the value of k_7) the more efficient is the phenol as an antioxidant for rubber[20].

Since the reactivity of an inhibitor towards a free radical is determined by the ease of abstraction of a labile hydrogen atom, those inhibitors that are active towards alkyl radicals may be active also towards peroxy-radicals. This suggestion is supported by published results[22,23].

A most important characteristic of stabilisers against oxidative degradation is their ability to decompose hydroperoxides by a molecular mechanism. The primary product of the oxidation of an organic compound is usually a hydroperoxide, which breaks down slowly into radicals capable of initiating oxidation chains, so that oxidation proceeds autocatalytically. Decomposition of the hydroperoxide by a stabiliser prevents such autocatalysis. The efficiency of a stabiliser can conveniently be assessed on a model reaction with a simple hydroperoxide (of cumene, tetralin, etc.). A correlation was shown[22] between the half-decomposition time of cumene hydroperoxide and the induction period in the oxidation of rubbers in the presence of various antioxidants. Another important parameter is the yield of radicals per hydroperoxide molecule decomposed. Increase in the rate of breakdown should be accompanied by a decrease in this yield: otherwise the test compound will catalyse the chain degradation.

The efficiency of a chemical compound in decomposing a hydroperoxide can be assessed quantitatively by two parameters—the ratios of reaction velocities and of yields of radicals in the absence and in the presence of this compound:

$$\frac{W}{W_x} < 1; \quad \frac{e}{e_x} = \frac{W_i/W}{W_{ix}/W_x} > 1$$

where W and W_x, W_i and W_{ix}, and e and e_x are the rates of breakdown, the rates of formation of radicals, and the yields of radicals in the absence and in the presence of the test compound respectively. The rate of decomposition can be determined by measuring by iodometric titration the decrease in the concentration of hydroperoxide with time. The method of inhibitors[29] (based on the induction period) or the chemiluminescence method[25] can be used to determine the rate of formation of radicals.

The effectiveness of a stabiliser is not always determined completely by its ability to terminate chains and to decompose hydroperoxides by a molecular mechanism. Its efficiency is diminished also by reaction of an inhibitor radical with a hydroperoxide molecule

$$ROOH + In\cdot \xrightarrow{k_{-7}} RO_2\cdot + InH . \qquad (10)$$

The role of this reaction will be significant if[30]

$$k_{-7} \cong \frac{2k_7k_8[InH]}{k_6[ROOH]}, \qquad (11)$$

where $k_8 = k_{t12}$ and $k_6 = k_{t11}$. In the oxidation of tetralin (at 65 °C) the rate constant k_{-7} reaches 10^4 M^{-1} s^{-1} for several aromatic phenols[31]. It can be shown that Eqn. (11) is satisfied with such values of k_{-7}. The role of reaction (10) can be assessed if the model oxidation is conducted in the presence of a certain quantity of a hydroperoxide.

The relative simplicity of the procedures and the possibility of evaluating rate constants enable model reactions to be used for the rapid quantitative assessment of various classes of compounds as potential stabilisers[20-23,32]. In several cases model reactions made it possible to establish the mechanism of the action of antioxidants[28,33,34] and to elucidate the nature of synergism[33,35,36].

The above advantages of model reactions of simple compounds are accompanied by the substantial defect of not reflecting the specific character of processes occurring in macromolecular compounds. Unfortunately, the mechanism of the degradation of polymers has not yet been sufficiently studied to enable these processes to be used as models. The initiated oxidation of molten polyethylene of low molecular weight[37] and that of solid isotactic polypropylene[38] have been most thoroughly studied in this respect. Kinetic results obtained in this work can be used to assess the effectiveness of compounds as stabilisers. Radical polymerisation at high degrees of conversion can be used as macromolecular model reaction with an active centre (the radical R·) to assess the efficiency of thermostabilisers[18,39].

III. ACCELERATED TRIALS OF STABILISERS

Although model reactions and reactions in polymers have much in common, stabilisers selected on the basis of model reactions require further verification of their

† The coefficient f may vary within wider limits, e.g. with inhibitors containing several functional groups.

effectiveness in the polymers themselves or in polymeric materials. This is because the efficiency of a stabiliser in a polymer is appreciably determined by several additional physicochemical factors, the most important of which are (i) the chemical stability of the stabiliser itself (with respect to the action of heat, oxygen, certain additives, etc.), (ii) the compatibility of the stabiliser with the polymer, and (iii) the effect of the solid phase on the reactivity of the stabiliser. The best method for finally assessing the efficiency of a stabiliser is, of course, to test it in the polymer under service conditions. In many cases, however, such trials last an extremely long time (for months and even years). This period can be shortened either by raising the temperature (in the cases of thermal and oxidative degradation) or by increasing the pressure of oxygen (in the case of oxidative degradation)[20].

Since polymers and polymeric materials are complicated systems, the effectiveness of stabilisers in accelerated trials is determined by the use of general mechanical and physicochemical parameters to characterise the progress of degradation. The former include elasticity, strength, etc. Among physicochemical parameters we may note viscosity and solubility, quantity of oxygen absorbed and induction period, decrease or increase in weight, thermal effects, and change in pressure caused by the evolution of simple degradation products. Definite interrelationships should clearly exist in the variation of these parameters during degradation. In the thermo-oxidative degradation of polypropylene, for example, the rate curves for viscosity, breaking load, elongation, and oxygen absorption are of the same type[40], with the most rapid changes in these parameters occurring simultaneously.

Thus two sets of methods—preliminary assessment of effectiveness in model reactions and accelerated trials in polymers—are used to test chemical compounds as stabilisers. Both sets of methods should be quite rapid, and they should give mutually consistent results for assessing the efficiency of the stabilisers and ascertaining the mechanism of their stabilising effect.

IV. SCHEME OF TESTING

It is advisable to use the well studied polymerisation of styrene and oxidation of cumene as model reactions. The rate of initiation by azoisobutyronitrile (Aibn) is calculated by means of the formula

$$W_i = ek_d[\text{Aibn}],$$

where the rate of decomposition of the initiator

$$k_d = 1.58 \times 10^{15} \exp(-30800/RT)$$

varies slightly with the nature of the solvent[41,42]‡. The yield of radicals e is close to 1.2 for aromatic hydrocarbons[43]; its values for styrene and cumene are respectively 1.1–1.2 [44,45] and 1.1,[29] and we can adopt with sufficient accuracy $e \simeq 1.1$ for both compounds§.

‡ This value of the rate constant is identical with the average value in aromatic solvents[27].

§The yield of radicals for cumene varies[29] from 1.0 to 1.25 with rise in temperature from 40 to 80°C (the temperature range normally employed for azoisobutyronitrile as initiator), so that the average value of the yield 1.1 can be adopted for all temperatures.

The method of purification described in Ref. 46 was used for styrene, and those of Ref. 42 for cumene and azoisobutyronitrile. Cumene hydroperoxide free from inhibiting impurities can be prepared relatively simply[47]. The rates of reaction of the purified specimens should approximately satisfy Eqn. (4). The rate constants of chain propagation and termination have the values—for styrene¶

$$k_{p11} = k_p = 10^{5.7} \exp(-6000/RT)\ \text{M}^{-1}\ \text{s}^{-1};$$

$$k_t = k_0 = 10^{7.9} \exp(-2000/RT)\ \text{M}^{-1}\ \text{s}^{-1};$$

and for cumene[48]†

$$k_{p11} = k_3 = 10^{6.67 \pm 0.34} \exp[-(9800 \pm 400)/RT]\ \text{M}^{-1}\ \text{s}^{-1};$$

$$k_t = k_6 = 10^{9.2 \pm 0.3} \exp[-(6000 \pm 300)/RT]\ \text{M}^{-1}\ \text{s}^{-1};$$

The rate of polymerisation of styrene can conveniently be determined dilatometrically[18], and the rate of oxidation of cumene from the absorption of oxygen[20,49]. Previous studies[47,50] have shown that the rate of decomposition of cumene hydroperoxide (at relatively low concentrations [ROOH] < 0.1 M) into cumene and the rate of breakdown into radicals can be calculated by means of the formulae

$$W = k_d \cdot [\text{RH}][\text{ROOH}],$$

$$W_i = k_i[\text{RH}][\text{ROOH}],$$

where

$$k_d = 1.1 \times 10^8 \exp(-25400/RT)\ \text{M}^{-1}\ \text{s}^{-1},$$

$$k_i = 10^8 \exp(-26200/RT)\ \text{M}^{-1}\ \text{s}^{-1}.$$

Thus two of the four reaction velocities required to characterise the ability of a test compound to decompose the hydroperoxide can be calculated (in the absence of the test compound) from published data.

The oxidation of molten polyethylene and solid isotactic polypropylene can be used as polymeric model reactions of oxidative degradation. In molten polyethylene the cumene peroxide used as initiator decomposes into radicals over the temperature range 110–145°C with[37]

$$k_i = 10^{13.5 \pm 1.0} \exp[-(32000 \pm 2000)/RT]\ \text{s}^{-1}.$$

The rate constant determined[51] in solid polypropylene at 114°C was identical with the value[52] in solid polyethylene at this temperature. It may be postulated that the rate constants for breakdown into radicals coincide over the temperature range 114–128°C, for which it was found in polyethylene that

$$k_i = 8.5 \times 10^{15} \exp(-37500/RT)\ \text{s}^{-1}.$$

Specimens of polyethylene and polypropylene purified as in Refs. 37 and 52 had the following relations between propagation and termination rate constants—for polyethylene[37]

$$k_3/k_6^{1/2} = 10^{2.7 \pm 0.5} \exp[-(11000 \pm 1000)/RT]\ \text{M}^{-1/2}\ \text{s}^{-1/2}.$$

and for polypropylene[38]

$$k_3/k_6^{1/2} = 2.7 \times 10^6 \exp(-13500/RT)\ \text{M}^{-1/2}\ \text{s}^{-1/2}.$$

Rates of oxidation of polyethylene and polypropylene are determined from the absorption of oxygen[37,38].

The model chain reactions—the polymerisation of styrene and the oxidation of cumene, molten polyethylene,

¶ Calculated from results obtained by Bamford, Dewar, and Burnett, cited in Ref. 15.

† Rate constants for cumene taken from Ref. 48 coincide within the limits of accuracy indicated with the constants obtained by other workers[27].

and solid polypropylene—can be represented by the same general scheme (reactions 1–3), so that the same criteria are used to assess the effectiveness of test compounds. A general criterion is the ratio W/W_X of the reaction velocities in the absence and in the presence of the compound. For inhibitors this ratio is related to the kinetic parameters of the model reactions by Eqn. (9). The minimum value at which the test compound is a potential stabiliser can be taken as $fk_{p21} = 100\ M^{-1}\ s^{-1}$, which is roughly 10% of the inhibition rate constants for weak inhibitors[14,27]. Antioxidants possessing little inhibiting activity may be of interest if they decompose hydroperoxides as well as terminating chains[33].

Quantitative assessment of thermostabilisers can be based on the macromolecular polymerisation of methyl methacrylate and acrylonitrile to high degrees of conversion[39], at which the lifetimes of the radicals R· amount to tens of minutes. Thus a certain concentration of these radicals can be produced relatively simply (by photoinitiation and by thermal initiation), and then the kinetics of their decay on the test compound

$$-\frac{d[R^{\cdot}]}{dt} = k_z[R^{\cdot}][InH].$$

can be observed. Integration of this equation yields

$$\ln\frac{W_0}{W} = k_z[InH]t, \qquad (12)$$

in which W_0 is the rate of the reaction in the absence of the test compound and W the rate of reaction at time t after cessation of initiation. This shows that the inhibition rate constant k_Z can be determined directly from the measured reaction rates W and W_0. The techniques of the accelerated testing of polymers have been described in the literature[3,20,21,53–58].

V. EXPERIMENTAL RESULTS OBTAINED BY TEST SCHEME

The effectiveness of a series of stabilisers can be compared from experimental results obtained from model reactions on simple compounds and from accelerated tests on polymers[2]. Table 1 lists data on the oxidation of molten polyethylene and on the polymerisation of styrene in the presence of four stabilisers. The sequence of inhibiting effects is maintained, although the stabilisers interact with different active centres in each model reaction.

Table 1. Inhibiting effect W/W_X of stabilisers in the oxidation of molten polyethylene and the polymerisation of styrene*.

Stabiliser	Oxidation of molten polyethylene at 135°C ($10^7 W_i$ = 4.6 M s^{-1}) initiated by dicumenyl peroxide	Polymerisation of styrene in presence of oxygen at 100°C ($10^7 W_i$ = 4.4 M s^{-1}) initiated by butylphenyltriazen	Polymerisation of styrene at 100°C ($10^7 W_i$ = 4.4 M s^{-1}) initiated by butylphenyltriazen
Diphenylamine	2	1.5	1.0
Phenyl-2-naphthylamine (Neozone D)	10	4	1.2
2,6-Di-t-butyl-4-methylphenol (Ionol)	>100	>50	10
Methylenebis-2-(6-t-butyl-4-methylphenol (2246)	>100	>50	10

* When styrene undergoes polymerisation in the presence of oxygen, most of the R· radicals are converted into RO_2· radicals.

Table 2 gives data on the inhibiting effects of three stabilisers, obtained in a model reaction and in accelerated trials on rubbers. Stronger chain-reaction inhibitors produce longer induction periods in the oxidation of the rubber. It is evident also that the peak on the differential thermal analysis curve undergoes a larger displacement to higher temperatures in the presence of a stronger stabiliser (*NN'*-diphenyl-*p*-phenylenediamine). Thus results obtained on a model reaction agree well with those of accelerated trials of these stabilisers on polymers.

Table 2. Comparison of inhibiting effects of stabilisers on a model reaction and in accelerated tests on polymers.

Stabiliser	W/W_X in polymerisation of styrene in presence of oxygen at 100°C ($10^7 W_i$ = 4.4 M s^{-1}) initiated by butylphenyltriazen	Induction period in the oxidation of SKS-30ARK rubber at 130°C, min	Shift ΔT of peak on d.t.a. curve for SKD rubber
2,6-Di-t-butyl-4-methylphenol (Ionol)	>50	760	–
NN'-Diphenyl-*p*-phenylenediamine	50	390	83
Phenyl-2-naphthylamine (Neozone D)	4	200	9

Table 3. Comparison of rates of decomposition of cumene hydroperoxide for several stabilisers with their antioxidant behaviour in rubber.

Stabiliser	Ratio $W_X W$ of rates of decompn. of cumene hydroperoxide in presence and in absence of stabiliser at 130°C	Induction period in oxidation of SKI–3 rubber at 130°C
NN'-Di-2-naphthyl-*p*-phenylenediamine (Age-Rite White)	1.0	900
NN'-Diphenyl-*p*-phenylenediamine	1.1	900
N-Isopropyl-*N'*-phenyl-*p*-phenylenediamine (4010)	1.8	780
Methylenebis-2-(6-t-butyl-4-methylphenol) (2246)	3.0	360
Trisnonylphenyl phosphite (Polyguard)	30	48

Table 3 compares data on the rates of decomposition of cumene hydroperoxide in the presence of several stabilisers with their effectiveness (based on the induction period) as antioxidants for rubber. This induction period is found to decrease with increase in the rate of decomposition of the hydroperoxide. The stabilising effects of these compounds are evidently based solely on the ability to terminate chains in the oxidation of rubber. In respect of hydroperoxide decomposition the compounds are catalysts of rubber oxidation. For this reason methylenebis-2-(6-t-butyl-4-methylphenol) is a weaker stabiliser (according to the induction period) than is *NN'*-diphenyl-*p*-phenylenediamine, in spite of having a larger inhibition parameter in the model polymerisation of styrene (Tables 1 and 2).

Thus the experimental results obtained in the above scheme of testing show good correlation between test data on model reactions and accelerated trials of chemical compounds on polymers. This permits the use of model

reactions for the rapid selection of potential stabilisers from a large number of test compounds. Furthermore, as already noted, model reactions yield information on the mechanism of the stabilising effect in terms of primary reactions.

The results indicate also a correlation between accelerated trials on stabilisers and their stabilising effects in polymers under natural conditions. Thus the test results show that derivatives of *p*-phenylenediamine should be most effective antioxidants, as is indeed observed with most rubbers[22].

VI. QUANTITATIVE RESULTS ON ANTIOXIDANT STABILISERS OBTAINED BY MEANS OF MODEL REACTIONS

Consideration has been given[3] to optimum reaction conditions for the model initiated oxidation of cumene permitting by means of Eqn. (9) the evaluation of fk_7 (fk_{p21}) in the range 10^2–10^5 M^{-1} s^{-1} at 40, 60, and 80°C. If the stabiliser is an inhibitor and is consumed only in terminating chains, the duration of its action (the induction period) is

$$\tau = \frac{f\,(\mathrm{InH})}{W_i} \quad . \tag{13}$$

This formula can be used to find the coefficient f from the experimental induction period. For any time t we can write

$$\frac{f\{[\mathrm{InH}]_0 - [\mathrm{InH}]\}}{W_i} = t \quad . \tag{14}$$

Substituting in (8) for [InH] from (14) and integrating, we obtain for the early stages of conversion the relation[59]

$$\frac{[O_2]}{[RH]} = -\frac{k_3}{k_7}\ln\left(1 - \frac{t}{\tau}\right), \tag{15}$$

where k_3 (k_{p11}) is the rate constant of chain propagation.

Table 4. Rate constants k_7 for reaction of peroxy-radicals with inhibitors and inhibition coefficients f.

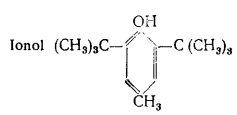
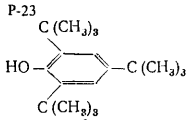
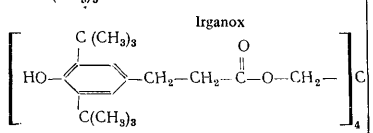
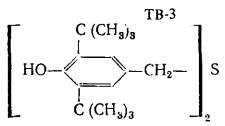
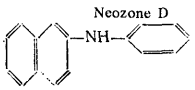
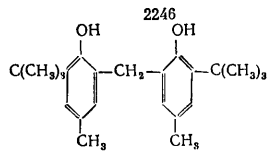
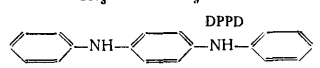
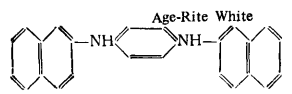
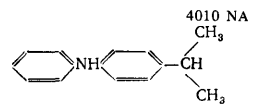
Inhibitor	Peroxy-radical	Temp., °C	lg [(k_7)60°C, M^{-1} s^{-1}]	Pre-exponential factor, lg A	E, kcal mole^{-1}	f per independent inhibiting group
Ionol 	cumene	40–80	4.34±0.03	7.27±0.32	4.46±0.49	2.1±0.1
P-23 	»	»	4.33±0.02	7.25±0.18	4.46±0.28	2.1±0.2
Irganox 	»	»	4.17±0.03	7.23±0.32	4.68±0.49	2.1±0.2
TB-3 	»	»	4.26±0.03	7.30±0.31	4.63±0.47	2.4±0.1
Neozone D 	»	»	4.83±0.03	7.03±0.39	3.34±0.60	2.0±0.2
2246 	»	»	5.60±0.05	7.09±0.66	2.28±1.0	2.0±0.1
DPPD 	»	»	5.34±0.09	—	—	2.0±0.1
Age-Rite White 	»	»	5.44±0.08	—	—	2.2±0.3
4010 NA 	»	»	5.83±0.05	7.32±0.64	2.77±0.98	2.0±0.04

Table 4 (contd.)

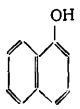
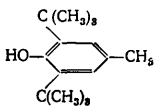
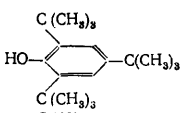
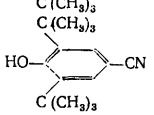
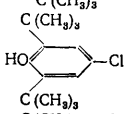
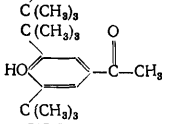
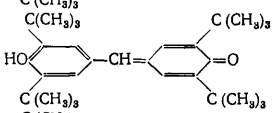
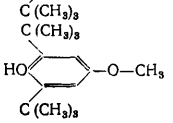
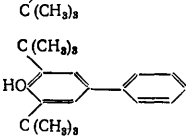
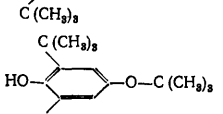
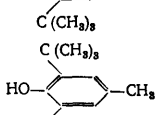
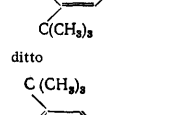
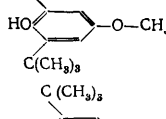
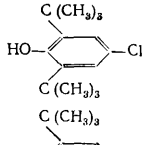
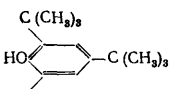
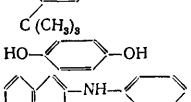
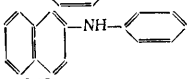
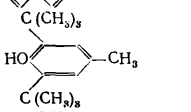
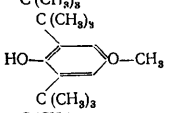
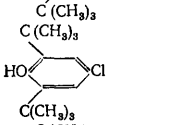
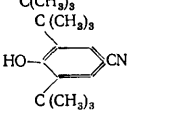
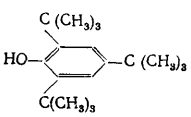
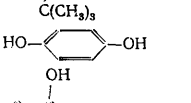
Inhibitor	Peroxy-radical	Temp., °C	lg [(k_7)60°C, M^{-1} s^{-1}]	Pre-exponential factor, lg A	E, kcal mole^{-1}	f per independent inhibiting group
	»	»	5.27±0.04	—	—	2.1±0.2
	»	»	5.29±0.09	—	—	2.0
	ethylbenzene*	40—70	4.31±0.02	7.52±0.22	4.90±0.33	—
	ethylbenzene*	40—70	4.19±0.02	6.90±0.12	4.12±0.18	—
	»	»	3.19±0.03	6.89±0.12	5.64±0.18	—
	»	»	3.92±0.02	7.20±0.12	5.00±0.18	—
	»	»	3.34±0.02	7.22±0.13	5.92±0.20	—
	»	»	4.45±0.02	7.0±0.18	3.90±0.28	—
	»	»	5.19±0.02	7.53±0.17	3.57±0.26	—
	»	»	4.27±0.03	7.48±0.33	4.90±0.50	—
	»	»	4.69±0.03	7.54±0.26	4.37±0.39	—
	styrene	13—50	4.25	—	—	—
ditto	»	»	$(4.25)_{65°C}$	—	—	—
	»	»	$(4.89)_{65°C}$	—	—	—
	»	»	$(3.83)_{65°C}$	—	—	—
	»	»	$(3.23)_{65°C}$	—	—	—

Table 4 (contd.)

Inhibitor	Peroxy-radical	Temp., °C	lg [(k_7)60°C, M^{-1} s^{-1}]	Pre-exponential factor, lg A	E, kcal mole^{-1}	f per independent inhibiting group
	styrene	13—50	$(4.21)_{65°C}$	—	—	—
	»	»	$(5.31)_{65°C}$	—	—	—
	»	»	$(4.70)_{65°C}$	—	—	—
	tetralin	50	4.43	—	—	—
	»	65	4.95	—	—	—
	»	65	3.92	—	—	—
	»	65	3.20	—	—	—
	»	»	4.45	—	—	—
	»	50	4.88	—	—	—
	»	50	4.86	—	—	—

* Experiments made in chlorobenzene with an equal volume of ethylbenzene.

Investigation of several known stabilisers in the model oxidation of cumene established that the rate curves for the absorption of oxygen in their presence are well linearised when plotted in the coordinates of Eqn. (15). This implies that the stabilisers inhibit the reaction in conformity with the simple scheme considered above‡. Hence the coefficients f and the inhibition rate constants can be determined by means of Eqns. (13) and (15). Table 4 lists values of k_7 and f for the stabilisers studied (rate constants were computed per inhibiting group). It includes for comparison values of k_7 obtained for various antioxidants on reaction with peroxy-radicals of ethylbenzene[61], styrene, and tetralin[27]. The inhibition coefficient f per independent inhibiting group is ~2 for all the stabilisers. This means that radicals formed from antioxidants react only with peroxy-radicals of cumene and do not interact.

Comparison of the rate constants for the reaction of any one inhibitor (2,6-di-t-butyl-4-methylphenol, its three derivatives in which the 4-methyl has been replaced by cyano, chloro, and methoxy; tri-t-butylphenol, *N*-phenyl-2-naphthylamine, 1-naphthol, or quinol) with various peroxy-radicals shows that k_7 is almost independent of the structure of the latter, as already noted above. The maximum difference does not exceed a factor of two, which may be largely due to experimental error, since the values of k_7 under comparison were obtained by different methods. Such independence of k_7 is of great interest in connection with testing, since it permits the choice of model reactions that have been most thoroughly studied and that are simplest to conduct.

Comparison of the rate constants k_7 for *para*-substituted 2,6-di-t-butylphenols shows a slight variation in reactivity of the inhibitor with the structure of the substituent provided that the latter contains an alkyl group directly attached to the benzene ring. The maximum deviation from the mean rate constant ($10^{4.30}$ at 60°C) does not exceed 30–70%. With the peroxy-radicals of cumene and ethylbenzene, for which rate constants have been determined most accurately, the maximum deviation from the mean ($10^{4.27}$) does not exceed 25%. Inspection of published data[27] shows that the rate constants k_7 obtained for various peroxy-radicals and derivatives of phenol having analogous *para*-substituents also have closely

‡This result is not self-evident, since inhibited oxidation has in general a complicated mechanism. A detailed survey has been made[60] of the general scheme of inhibited oxidation and published experimental results.

similar values (independently of other alkyl substituents). Only 7 of the 60 values of k_7 cited in Ref. 27 exhibit deviations from the mean exceeding a factor of 2.5, and the mean rate constant ($10^{4.35}$ at 60°C) is almost identical with the mean for 2,6-di-t-butylphenol derivatives.

Considerable variation in the rate constant k_7 is observed only in the presence of strong electron-donating or -accepting substituents[61]. Thus the σ-constants for 4-methoxyl, 4-cyano, and 4-methyl are respectively −0.776, +0.628, and −0.170. According to Table 4 the rates of reaction of the peroxy-radical of ethylbenzene with 2,6-di-t-butylphenol containing in the 4-position respectively hydroxymethyl, methyl, and cyano are in the ratios 100 : 10 : 1. Jaffe's well known review[62] gives σ-constants for many *p*-alkyl substituents and for various *para*-substituents with the alkyl directly attached to the benzene ring. The maximum difference in the σ-constants of these substituents does not exceed 0.5, which corresponds to an approximately sixfold difference in rate constants k_7 or a deviation from the mean by a factor of 2.5.

Thus the variation in the σ-constants for derivatives of phenol *para*-substituted with groups having weak donor–acceptor properties corresponds on the whole to the variation in the rate constants k_7. It is noteworthy that the pre-exponential factors in the inhibition rate constants are almost identical within the limits of experimental accuracy independently of the structure of the peroxy-radical or the nature of the antioxidant. Thus in reactions with peroxy-radicals of cumene and of ethylbenzene these factors are respectively $10^{7.21\pm0.11}$ and $10^{7.25\pm0.27}$. We can write for both series the general formula

$$k_7 = 10^{7.23\pm0.19}e^{-E/RT} \qquad (16)$$

for the inhibition rate constant, where 0.19 gives the standard deviation. We can use (16) to determine the activation energy if we know the rate constant at a single temperature; an error of a factor of two in this rate constant gives an error in the activation energy of only ±0.5 kcal mole^{-1}. Twelve inhibition rate constants are known[27] for the reaction of phenols with various peroxy-radicals. The mean pre-exponential factor in these constants is $10^{7.20}$, which coincides within the limits of experimental accuracy with the above value in Eqn. (16). This fact strongly suggests that experimental error is responsible for the compensating effect in these reactions observed between the pre-exponential factor and the activation energy[27], reaching 2 kcal mole^{-1} (more than a factor of ten in the pre-exponential factor).

Table 5. Rate constants of gas-phase radical substitutions involving relatively large radicals and molecules.

Reaction	Pre-exponential factor, lg (A, M^{-1} s^{-1})	E, kcal mole^{-1}
$NO+O_3\longrightarrow NO_2+O_2$	8.83±0.15	2.45±0.17
$C_2HCl_4+Cl_2\longrightarrow C_2HCl_5+Cl$	8.71±0.03	5.15±0.03
$C_2H_3Cl_2+Cl_2\longrightarrow C_2H_3Cl_3+Cl$	8.78±0.03	0.96±0.04
$CH_3+CH_3CHO\longrightarrow CH_4+CH_3CO$	8.86±0.16	7.50±0.30

Hardly any sufficiently accurate data have yet been published on rate constants for other radical substitutions in the liquid phase. Only two rate constants of chain propagation can be cited, for the liquid-phase oxidation of cumene and ethylbenzene: the first was given[48] as $10^{6.67\pm0.26}\exp[-(9800\pm400)/RT]$; the second can be obtained from the refined value[63] of the recombination rate constant for peroxy-radicals of ethylbenzene[61] as $10^{6.64\pm0.24}\exp[-(9550\pm360)/RT]$. The two constants have the same pre-exponential factor, differing from that in formula (16) by only slightly more than the experimental error.

A considerably greater quantity of accurate data are available on rate constants for radical substitution in the gas phase[64]. Table 5 gives the most accurate values for reactions involving relatively large radicals and molecules. The pre-exponential factors evidently coincide within the limits of experimental accuracy. The rate constant can in general be written

$$k = 10^{8.80\pm0.07}e^{-E/RT}. \qquad (17)$$

If the frequency of collisions in the gas is taken to be 2×10^{11} M^{-1} s^{-1},[65] the steric factor becomes 0.003. If we write the reaction rate constant in the logarithmic form

$$E = \theta\lg A - \theta\lg k, \qquad (18)$$

where $\theta = 0.004575\,T$ kcal mole^{-1}, and compare the resulting expression with the well known Polanyi–Semenov relation

$$E = B \pm \alpha Q,$$

we obtain, with a constant pre-exponential factor, the general formula

$$k = Ae^{-\frac{B}{RT}}e^{\pm\frac{\alpha Q}{RT}}, \qquad (19)$$

for the rate constant, where $A\exp(-B/RT)$ is the exchange rate constant ($Q = 0$). The relation linking the rate constant with the heat of reaction may be satisfied for reactions in which the pre-exponential factor and the coefficient α are constant. For a series of reactions involving the same radical, with the resonance energy of the radicals neglected, Eqn. (19) can be written in the form

$$\pm(D_0 - D) + \frac{\theta}{\alpha}\lg k - \frac{\theta}{\alpha}\lg k_0 = 0, \qquad (20)$$

where D and D_0 are the bond energies for the abstractable atom in the series of reactions and for exchange ($Q = 0$) in this series, and k_0 is the exchange rate constant. It follows from (20) that a linear dependence should exist between the logarithm of the rate constant and the bond energy. This is supported by published data.

The diagram illustrates results obtained[61] for the rate constants of reactions of the peroxy-radical of ethylbenzene with sterically hindered phenols (Table 4) and the energies of the hydrogen–oxygen bond in the latter (line *1*), together with corresponding results for reactions of the sodium atom with chlorinated methanes (involving detachment of a chlorine atom and formation of sodium chloride) (line *2*), reaction rate constants for the latter series and carbon–chlorine bond energies being taken from Refs. 64 and 66. Both series comprise exothermic reactions, so that formula (20) becomes

$$D = D_0 - \frac{\theta}{\alpha}\lg k + \frac{\theta}{\alpha}\lg k_0. \qquad (21)$$

The diagram shows good agreement between experimental results and Eqn. (21). The slopes of the straight lines show that α has the values 0.40 and 0.65 for reactions of the peroxy-radical with phenols and for those of sodium with chlorinated methanes respectively. The intercepts made on the D-axis give bond energies of 94 and 96 kcal mole^{-1}: the former is close to the estimate[8] of 90 kcal

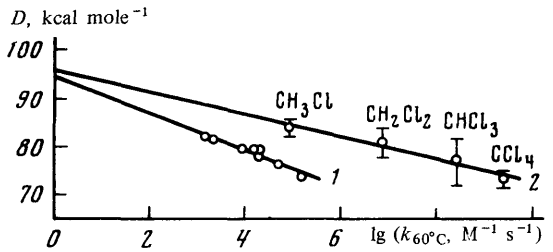
mole^{-1} for the hydrogen–oxygen bond energy in ethylbenzene hydroperoxide; the latter is almost identical with the sodium–chlorine bond energy[66] of 97.6 kcal mole^{-1}. These facts suggest that the exchange rate constants at 60°C for

$$RO'_2 + ROOH \rightarrow ROOH + RO'_2$$

and

$$Na + NaCl \rightarrow NaCl + Na$$

differ insignificantly from unity.



Linear relation between logarithm of rate constant at 60°C and bond energy of atom abstracted for series of radical substitutions of the same type: 1) liquid-phase reactions of the peroxy-radical of ethylbenzene with *para*-substituted 2,6-di-t-butylphenols; 2) gas-phase reactions of the sodium atom with chlorinated methanes.

Not all radical substitutions involving relatively large species have the above constant pre-exponential factors. In the liquid phase, for example, the rate constants for reaction of the diphenylpicrylhydrazyl radical with phenols[67] have factors of $10^{3.8-4.5}$, only one-thousandth of that in Eqn. (16). A low pre-exponential factor ($10^{3.2}$) is observed also in exchanges between sterically hindered phenoxy-radicals and phenols[67]. The low values evidently cannot be attributed to experimental error.

VII. QUANTITATIVE ASSESSMENT OF INHIBITORS IN VARIOUS COMPOSITIONS

Methods for the preliminary assessment of inhibitors on model reactions may be of general interest, since the kinetic characteristics obtained for the test compounds may be used in the investigation of chain processes occurring in hydrocarbons, foodstuffs, liquid perfumes, animal organisms, and plants. In the investigation of various compositions containing inhibiting agents it is possible to estimate the concentration of the inhibitor, establish the mechanism of its action, and determine the inhibition rate constant. Inhibitors present in lipid extracts of leaves and in petroleum have been analysed by means of the model oxidation of cumene[68,69]. Two inhibitors have been found in plants, with inhibition rate constants k_7 of 4000 and 120 000 M^{-1} s^{-1}; the second appears in the plant as winter approaches. The concentration of inhibitor—more precisely the value of $f[InH]$—in the dry extract is 0.06–0.3 mole kg^{-1}. Analysis of Western Siberian petroleum reveals four inhibitors, having inhibition rate constants of (30, 7.6, 1.4, and 0.73) $\times$ 10^4 M^{-1} s^{-1} and corresponding values of $f[InH]$ of 0.020, 0.015, 0.015, and ~0.015 mole kg^{-1}; the first three of these inhibitors are found in the asphaltenes, and the fourth occurs in the tars.

Thus both foliage and petroleum contain relatively high concentrations (0.01–0.1 mole kg^{-1}) of inhibitors. The most effective of these (with an inhibition rate constant of ~10^5 M^{-1} s^{-1}) can be assigned to the class of strongest inhibitors—antioxidants.

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