KINETICS OF DECOMPOSITION OF PEROXIDES CONTAINING FURANE CYCLE

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Introduction

The thermal decomposition of di-2-furoyl, di-5-bromo-2-furoyl, di-2-furil-ß-acryloyl peroxides and, for sake of comparison, dibenzoyl peroxide has been investigated in different types of solvents (benzene, dichloroethane, dioxan, ethyl acetate, methanol, acetic acid).

The overall decomposition of benzoyl peroxide is made up of a spontaneous cleavage- and radical- induced chain reactions (1):

spontaneous cleavage $\quad I \xrightarrow{k_d} 2\dot{R}$ *a)*

induced decomposition by $\dot{R}$ $\quad \dot{R} + I \xrightarrow{k_2} \dot{R} + \text{inactive product}$ *b)*

transfer of radical activity to solvent $\quad \dot{R} + SH \xrightarrow{k_3} \dot{S} + RH$ *c)*

induced decomposition by $\dot{S}$ $\quad \dot{S} + I \xrightarrow{k_4} \dot{R} + RS$ *d)*

termination $\quad \dot{R} + \dot{R} \xrightarrow{k_5} \text{inactive product}$ *e)*

$\dot{R} + \dot{S} \xrightarrow{k_6} \text{inactive product}$ *f)*

$\dot{S} + \dot{S} \xrightarrow{k_7} \text{inactive product}$ *g)*

In two cases: 1. in a completely inert solvent with which the $\dot{R}$ radicals cannot react and the significant type of induced decomposition would be $\dot{R} + I$ and the significant type of termination would be $\dot{R} + \dot{R}$, as well as 2. if the primary $\dot{R}$ radicals are rapidly converted to $\dot{S}$ radicals and if the reactions $\dot{S} + I$ and $\dot{S} + \dot{S}$ are the important induced decomposition step and termination step, respectively, the total rate of disappearance of peroxide is given by:

$$-\frac{d[I]}{dt} = k_d[I] + k_{\text{ind}}[I]^{3/2} \qquad (1)$$

where k_d denotes the specific rate of spontaneous cleavage,
k_{ind} the specific rate of induced decomposition.
This equation may be integrated to give

$$\ln\frac{a+[\mathrm{I}]^{1/2}}{[\mathrm{I}]^{1/2}}=\ln\frac{a+[\mathrm{I}]_0^{1/2}}{[\mathrm{I}]_0^{1/2}}+\frac{k_d t}{2} \tag{2}$$

which may be converted to the form

$$[\mathrm{I}]_1^{-1/2}=c[\mathrm{I}]_2^{-1/2}+\frac{c-1}{a} \tag{3}$$

where a — k_d/k_{ind}
t — time
$[\mathrm{I}]_{10}$ and $[\mathrm{I}]_{20}$ — different initial peroxide concentrations of two runs
$[\mathrm{I}]_1$ and $[\mathrm{I}]_2$ — peroxide concentrations at equal times in the two runs.

Experimental

The preparation and purification of peroxides, applied solvents and other types of chemicals were described in our previous papers (2,3,4). Solutions of peroxides made up in volumetric flasks were pipetted into ampoules, the ampoules frozen in a dry ice—acetone bath, then evacuated and flushed repeatedly with purified nitrogen, warmed to room temperature, again evacuated and flushed repeatedly with purified nitrogen and sealed off. The sealed ampoules were warmed to room temperature and then immersed int the thermostat for the specified times. The decompositions were continued up to 60 to 70%. The peroxide concentrations were determined both by the polarographic method (2,3,4) and iodometrically. The peroxide concentration values determined by the polarographic method and those determined iodometrically seldom differed by more than ±1%.

Results and discussion

The logarithm of peroxide concentration vs. time gave straight lines (except two cases discussed below) (Fig. 1). But the values k_{dl} calculated from the slopes of the plots of log [I] vs. time increased definitely with increasing initial peroxide concentration in a given solvent (except acetic acid and methanol in which the decomposition of peroxides containing furane cycle is the quickest) and varied considerably in magnitude from one solvent to another (Tables 1 through 4). These facts indicate that, as in the case of benzoyl peroxide, the unimolecular cleavage of the peroxides containing furane cycle is accompanied by a higher- order reaction. No effective separation of the in-

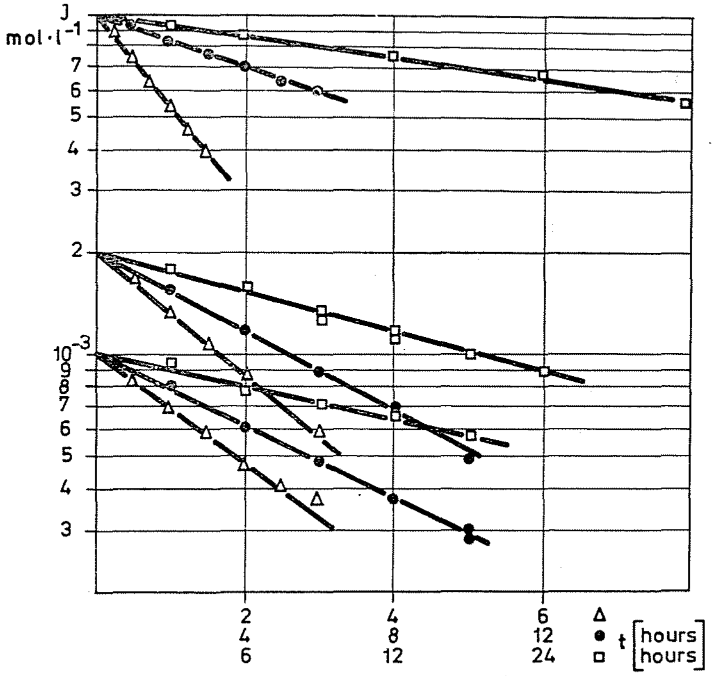


Fig. 1. Furoyl peroxide decomposition in dichloroethane. △: 80 °C; ●: 70 °C; □: 60 °C

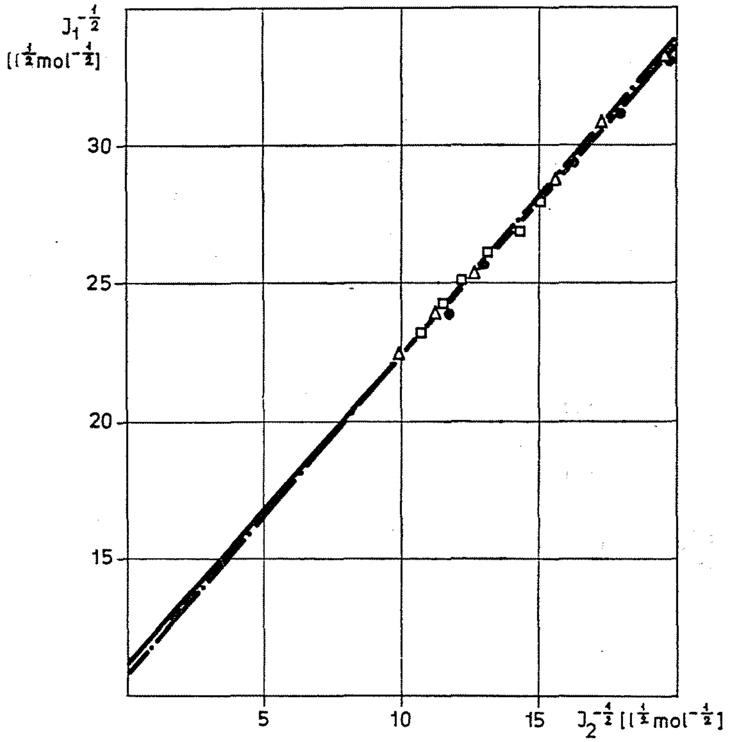


Fig. 2. Plots of $[I]_1^{-1/2}$ vs. $[I]_2^{-1/2}$ (Equ. 3) for furilacryloyl peroxide decomposition in benzene. △: 80 °C; ●: 70 °C; □ 60 °C

Table 1

Values of rate constants and activation energies of furoyl peroxide decomposition

Solvent	$k \cdot 10^6$	$I \cdot 10^3$ mol/l	80°	70°	60°	50°	40°	E kcal/mol
Benzene	k_{dl}	2	61	17.3	4.8			27.5
		10	97	26.9	7.4			30.0
	a		0.055	0.055	0.055			
	k_d	2	36	10.3	2.9			29.5
		10	36	10.3	2.9			
	k_{ind}		655	185	52.8			26.4
Dichloroethane	k_{dl}	1	107	34.0	10.1			27.6
		2	118	37.0	12.3			26.7
		10	171	48.7	18.3			26.9
	a		0.055	0.046	0.038			
	k_d	1	69.2	20.9	5.8			29.0
		2	70	19.6	5.7			
		10	70	18.7	5.8			
	k_{ind}		1270	425	151			27.9
Cyclohexane	k_{dl}	1	62	17.3	4.7			27.7
Dioxan	k_{dl}	2	144	46.5	15.5			26.0
		10	210					
	a		0.045					
	k_d	2	75.3					
		10	74					
	k_{ind}		1650					
Ethyl acetate	k_{dl}	2	79	23.2	6.5			29.2
		10	127					
	a		0.038					
	k_d	2	41					
		10	41					
	k_{ind}		1080					
Acetic acid	k_{dl}	2	1290	545	250	78.5		21.4
		10		605	265	85		
Methanol	k_{dl}	1			171	45.5	14.0	25.0

Where: k_d sec^{-1} rate constant of unimolecular decomposition of peroxide; k_{ind} $l^{\frac{1}{2}} \cdot mol.^{-\frac{1}{2}} sec^{-1}$ rate constant of induced decomposition; a — k_d/k_{ind}.

Table 2

Values of rate constants and activation energies of bromofuroyl peroxide decomposition

Solvent	$k \cdot 10^6$	$I \cdot 10^2$ mol/l	80°	70°	60°	50°	40°	30°	E kcal/mol
Benzene	k_{dl}	2	93.4	31.7	9.10				26.9
		10	150	50.5	16.30				25.9
	a		0.038	0.032	0.027				
	k_d	2	46	13.5	3.75				29.2
		10	46	13.5	3.75				
	k_{ind}		1210	422	141				25.1
Dichloroethane	k_{dl}	1	234	72.5	21.8				27.8
		2	247	80.0	23.0				27.8
		10	330	103	32.4				27.1
	a		0.038	0.033	0.029				
	k_d	1	110	35.7	9.4				27.8
		2	108	34.5	8.95				
		10	92	28.8	8.50				
	k_{ind}		2710	987	304				25.9
Cyclohexane	k_{dl}	1	94	32	9.2				26.8
Dioxan	k_{dl}	2	317	108	37				25.1
		10	551						
	a		0.019						
	k_d	2	102						
		10	102						
	k_{ind}		5280						
Ethyl acetate	k_{dl}	2	358	121.7	45				24.5
		10	684						
	a		0.01						
	k_d	2	68						
		10	69						
	k_{ind}		6850						
Acetic acid	k_{dl}	2		1154	460	270			19.5
		10		1160					
Methanol	k_{dl}	1				594	256	42.5	24.4

Where: k_d sec^{-1} rate constant of unimolecular decomposition of peroxide; k_{ind} l$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ sec^{-1} rate constant of induced decomposition; a — k_d/k_{ind}.

Table 3

Values of rate constants and activation energies for furilacryloyl peroxide decomposition

Solvent	$k \cdot 10^6$	$I \cdot 10^3$ mol/l	80°	70°	60°	50°	E kcal/mol
Benzene	k_{dl}	2	216	71.8	21.0		27.2
		10	384	128.2	39.8		26.4
	a		0.015	0.014	0.013		
	k_d sec^{-1}	2	65	20.0	5.6		28.6
		10	65	20.3	5.4		28.6
	k_{ind} $l^{\frac{1}{2}}. mol.^{-\frac{1}{2}} sec^{-1}$		4400	1450	440		26.9
Dichloroethane	k_{dl}	2		289	115.5	35.0	23.8
		10		510	192.0	71.0	23.0
	a			0.024	0.023	0.022	
	k_d sec^{-1}	2		112.3	39.2	12.4	24.5
		10		112.5	39.4	12.8	24.6
	k_{ind} $l^{\frac{1}{2}}, mol.^{-\frac{1}{2}} sec^{-1}$			4660	1730	593	22.6
Dioxan	k_{dl}	2	390	133	45.5		25.2
		10	668	234	80.4		25.3
	a		0.013	0.012	0.011		
	k_d sec^{-1}	2	99.3	29.2	9.5		27.3
		10	99.4	29.4	9.6		27.4
	k_{ind} $l^{\frac{1}{2}}. mol.^{-\frac{1}{2}} sec^{-1}$		7760	2550	895		25.8
Ethyl acetate	k_{dl}	2	430	142	54.5		24.4
		10	727	255	96.0		24.3
	a		0.013	0.012	0.011		
	k_d sec^{-1}	2	102	30.5	10.6		26.3
		10	102	30.7	10.8		26.4
	k_{ind} $l^{\frac{1}{2}}. mol.^{-\frac{1}{2}} sec^{-1}$		7950	2670	1010		24.2

Table 4

Values of rate constants and activation energies of benzoyl peroxide decomposition

Solvent	$k \cdot 10^6$	$I \cdot 10^3$ mol/l	80°	70°	60°	E kcal/mol
Benzene	k_{dl}	2	34.0	9.9	2.67	30.0
		20	34.0	9.9	2.67	30.0
	k_d		34.0	9.9	2.67	30.0
	k_{ind}		0	0	0	
Dichloroethane	k_{dl}	2	37.0	10.7	2.58	30.6
		20	45.5	13.4	3.57	29.3
	a		0.568	0.48	0.40	
	k_d	2	35.4	10.0	2.70	30.0
		20	35.6	10.5	2.66	
	k_{ind}		62.5	21.4	6.45	26.5
Cyclohexane	k_{dl}	2	41.6	11.5	3.25	29.8
	1	10	75.0	22.2	5.85	29.8
	a		0.034	0.030	0.024	
	k_d	2	19.0	6.2	1.28	32.0
		10	22.6	6.0	1.22	32.4
	k_{ind}		610	204	52.0	28.3
Dioxan	k_{dl}	2	113.1	39.0	12.35	25.8
		20	256.0	91.0	30.2	25.2
	a		0.026	0.023	0.021	
	k_d	2	43.7	13.8	4.40	26.9
		20	43.5	13.7	4.35	
	k_{ind}		1700	595	212	24.3
Ethyl acetate	k_{dl}	2	(71.0)	(24.8)	(6.65)	(27.6)
		20	105.0	40.2	10.70	26.7
	a		(0.114)	(0.10)	(0.09)	
	k_d	2	(51.9)	(17.7)	(4.60)	(27.6)
		20	(51.2)	(17.7)	(4.55)	
	k_{ind}		(450)	(177)	(51)	(25.4)
Acetic acid	k_{dl}	2	(60.0)	(22.1)	(6.25)	(26.5)
		20	96.0	38.6	11.70	24.6
	a		(0.098)	(0.075)	(0.56)	
	k_d	2	(42.2)	(14.1)	(3.80)	(27.8)
		20	(43.5)	(14.2)	(3.76)	
	k_{ind}		(436)	(190)	(67.5)	(22.6)
Methanol	k_{dl}	2	62.0	19.0	6.20	26.9

Where: k_d sec^{-1} rate constant of unimolecular decomposition of peroxide; k_{ind} $l^{\frac{1}{2}}$. mol.$^{-\frac{1}{2}}$ sec^{-1} rate constant of induced decomposition of peroxide; a — k_d/k_{ind}.

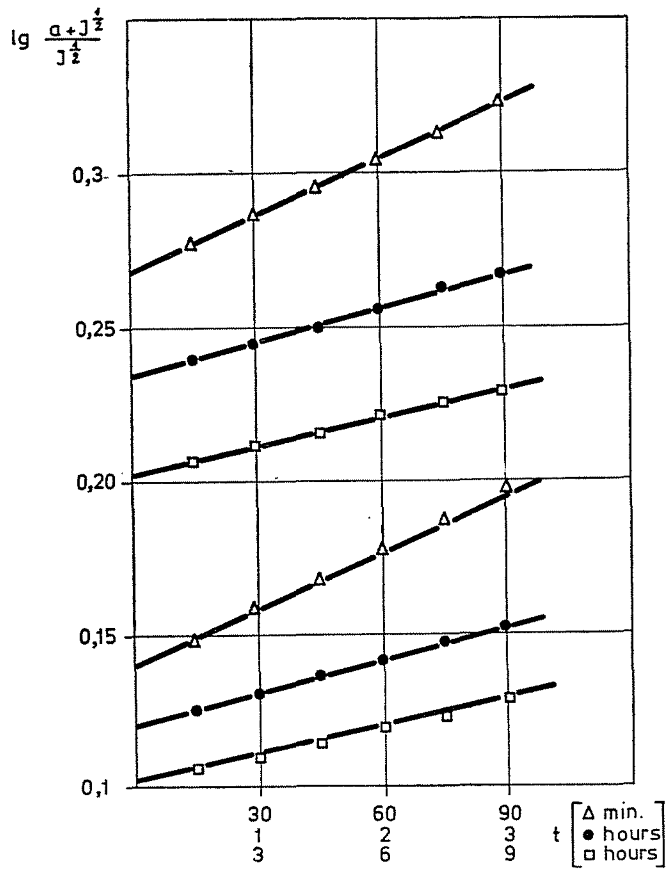


Fig. 3. Plots of log a + $[I]^{1/2}/[I]^{1/2}$ vs. time (Equ. 2) for bromofuroyl peroxide decomposition in benzene. △: 80 °C; ●: 70 °C; □: 60 °C; $[I]_0 = 2 \cdot 10^{-3}$ (up); $[I]_0 = 1 \cdot 10^{-2}$ (below)

duced decomposition from the primary process was possible by the use of such radical scavengers as styrene and methyl methacrylate, because the values of k_{dl} obtained in their presence also varied with the peroxide concentration and solvents. So we used the kinetic analysis method discussed above to determine the values of k_d and k_{ind}.

The plots of $[I]_1^{-1/2}$ vs. $[I]_2^{-1/2}$ gave straight lines (Fig. 2) from which a was calculated. The plots of log a + $[I]^{1/2}/[I]^{1/2}$ vs. time resulted in straight lines (Fig. 3) and k_d was determined from their slopes. The values of a and k_d together with values of k_{ind}, calculated from the relationship $k_{\text{ind}} = k_d/a$, are summarized in Tables 1 through 4.

It is interesting to note that the induced decomposition of the peroxides containing furane cycle seems to be most rapid even in such an inert solvent as benzene. On the other hand, the overall rate of decomposition in the solvents in which benzoyl peroxide decomposition was rapid (e. g. dioxan) appears

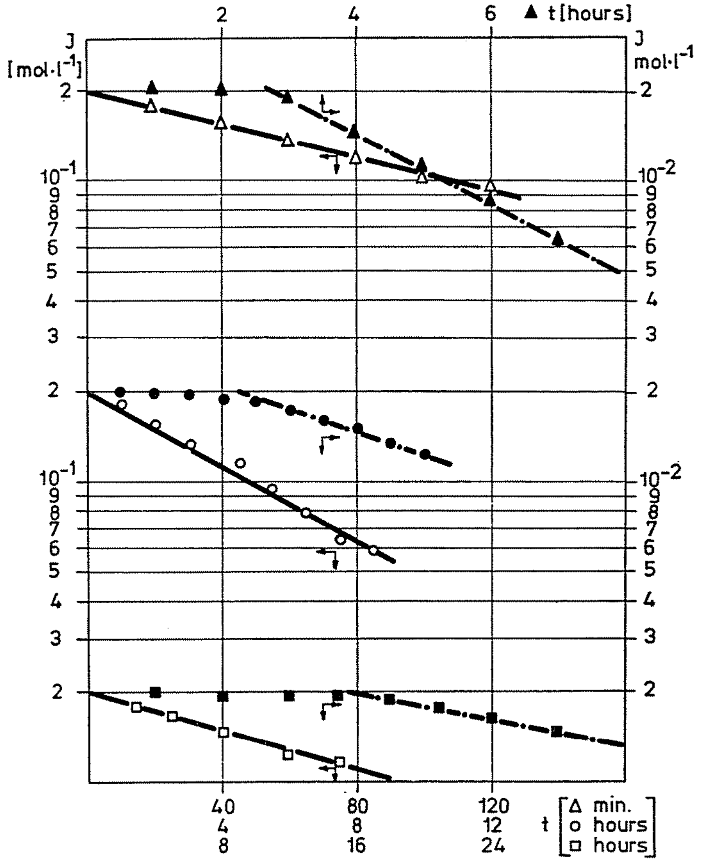


Fig. 4. Benzoyl peroxide decomposition in ethyl acetate. △: 80 °C; ○: 70 °C; □: 60 °C; $[I]_0 = 2 \cdot 10^{-2}$ mol/l; ▲: 80 °C; ●: 70 °C; ■: 60 °C; $[I]_0 = 2 \cdot 10^{-3}$ mol/l

to be similar for benzoyl and furoyl peroxides. These facts indicate that in the case of peroxides containing furane cycle reaction *b)* is more important than for benzoyl peroxide, but the reactions with the solvents in which benzoyl peroxide decomposition was rapid also seem to be operative at the same time.

Taking all the reactions *a)* to *g)* likely to be simultaneous, into consideration, the equation for the rate of decomposition becomes hopelessly complex. As certain reactions in the scheme discussed above must not be omitted, in order to obtain a simpler expression, some assumptions must be made about the relative rates of induced decompositions and termination reactions. Applying the assumption $k_4 = \sigma k_2$ and the geometric mean treatment often used in cases of radical chain reactions (5,6,7,8,9,10,11,12) which seem to be reasonable enough as far as there are no serious differences in the polarity of the reacting radicals, the application of the stationary-state condition to the radical concentrations leads to the equations:

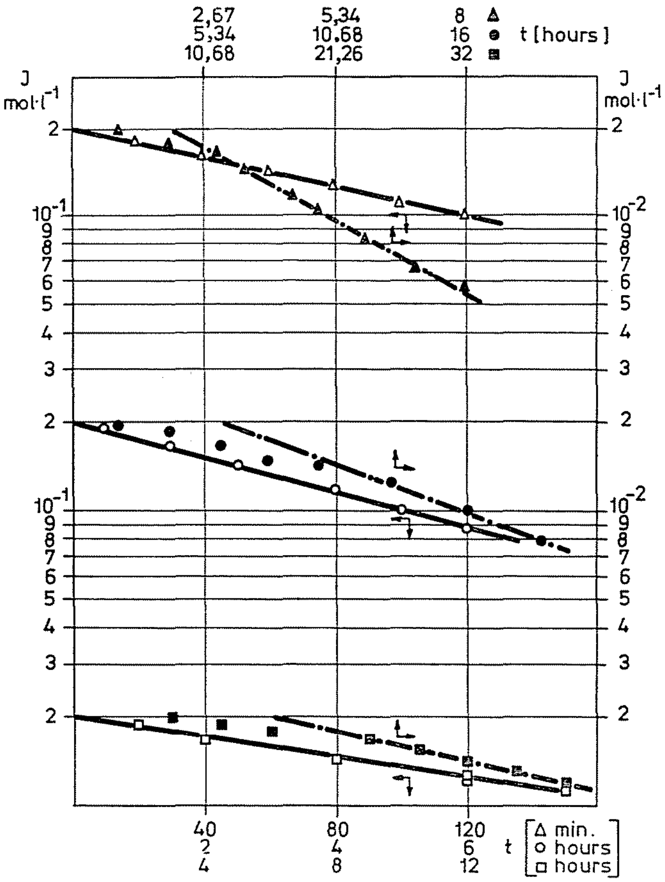


Fig. 5. Benzoyl peroxide decomposition in acetic acid. △: 80 °C; ○: 70 °C; □: 60 °C; $[\mathrm{I}]_0 =$ $= 2 \cdot 10^{-2}$ ml/l; ▲: 80 °C; ●: 70 °C; ■: 60 °C; $[\mathrm{I}]_0 = 2 \cdot 10^{-3}$ mol/l

$$\frac{d[\dot{\mathrm{R}}]}{dt} = 2k_d[\mathrm{I}] - k_3[\dot{\mathrm{R}}][\mathrm{SH}] + k_4[\dot{\mathrm{S}}][\mathrm{I}] - k_5[\dot{\mathrm{R}}]^2 - \sigma k_5[\dot{\mathrm{S}}][\dot{\mathrm{R}}] = 0$$

$$\frac{d[\dot{\mathrm{S}}]}{dt} = \qquad + k_3[\dot{\mathrm{R}}][\mathrm{SH}] + k_4[\dot{\mathrm{S}}][\mathrm{I}] - \sigma^2 k_5[\dot{\mathrm{S}}]^2 - \sigma k_5[\dot{\mathrm{S}}][\dot{\mathrm{R}}] = 0$$

$$-\frac{d[\mathrm{I}]}{dt} = k_d[\mathrm{I}] + k_2[\dot{\mathrm{R}}][\mathrm{I}] + \sigma k_2[\dot{\mathrm{S}}][\mathrm{I}] = k_d[\mathrm{I}] + k_2([\dot{\mathrm{R}}] + \sigma[\dot{\mathrm{S}}])[\mathrm{I}]$$

hence:

$$-\frac{d[\mathrm{I}]}{dt} = k_d\,[\mathrm{I}] + k_2(2k_d/k_5)^{1/2}[\mathrm{I}]^{3/2} = k_d[\mathrm{I}] + k_{\mathrm{ind}}[\mathrm{I}]^{3/2}.$$

It appears that this is the reason why our data seem to be in good agreement with the equations of NOZAKI and BARTLETT (1) and so the decomposition

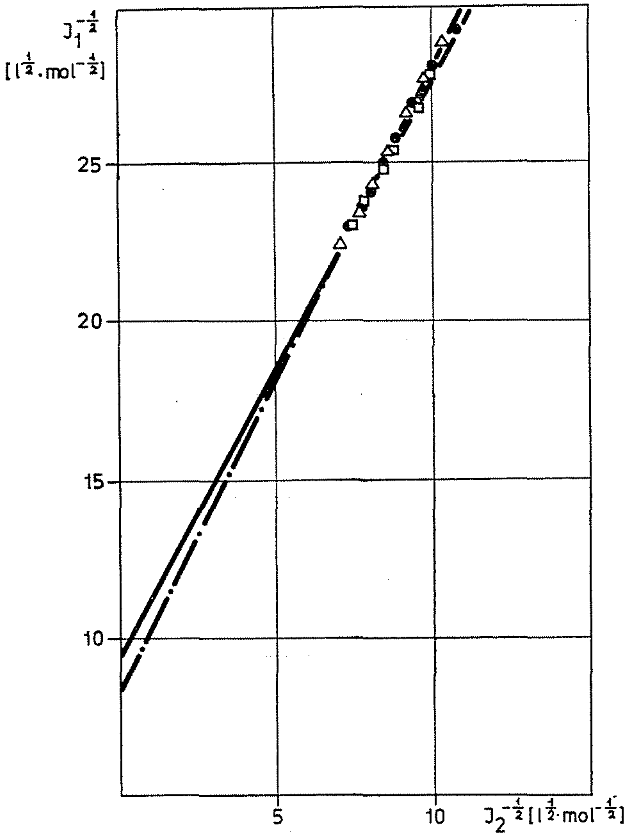


Fig. 6. Plots of $[I]_1^{-1/2}$ vs. $[I]_2^{-1/2}$ for benzoyl peroxide decomposition in ethyl acetate. △: 80 °C; ● : 70 °C; □: 60 °C

of these peroxides seems to prove the more general validity of the NOZAKI and BARTLETT equation.

The rapid decomposition of the peroxides containing furane cycle in acetic acid can be explained by the sensitivity of furane cycle to acids. The decomposition of furilacryloyl peroxide was extremely rapid in acetic acid and methanol.

Finally, there was still another problem concerning benzoyl peroxide decomposition in ethyl acetate and acetic acid. The logarithm of peroxide concentration vs. time gave straight lines only for $2 \cdot 10^{-2}$ mol/l initial peroxide concentrations. For $2 \cdot 10^{-3}$ mol/l initial benzoyl peroxide concentration initially the peroxide concentration did not decrease in ethyl acetate (Fig. 4); in acetic acid the initially slow decrease of peroxide concentration abruptly intensified (Fig. 5). Omitting the initial "induction period" belonging to the $2 \cdot 10^{-3}$ mol/l initial peroxide concentration, the plots of $[I]_1^{-1/2}$ vs. $[I]_2^{-1/2}$ gave straight lines (Figs 6, 7). The values calculated in this way are of course

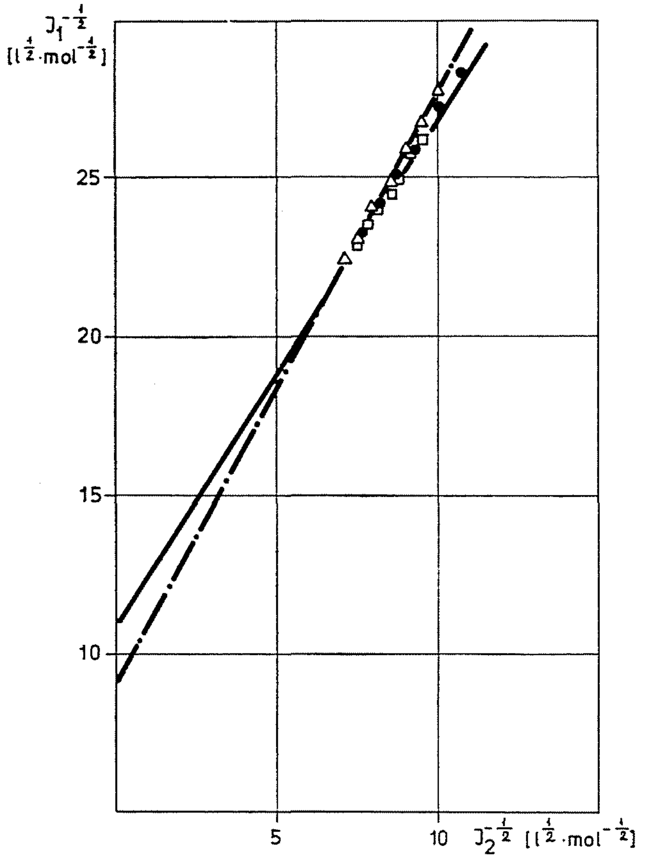


Fig. 7. Plots of $[I]_1^{-1/2}$ vs. $[I]_2^{-1/2}$ for benzoyl peroxide decomposition in acetic acid. △: 80 °C; ●: 70 °C; □: 60 °C

less reliable than those for other solvents, so they are put in brackets in Table 4. These discrepancies are likely to be attributable to the presence of a small amount of oxygen which could be eliminated only by using the vinyl acetate purification method (13) for ethyl acetate.

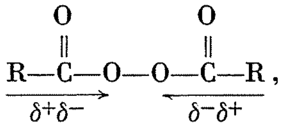
Summarizing the results, the following conclusions can be drawn:

1. The decomposition of the peroxides containing furane cycle seems to be essentially of the same complex nature as that of benzoyl peroxide, but the liability of these peroxides to induced decomposition appears to be higher.

2. The overall rate of decomposition of these peroxides seems to be high.

3. The values for the specific rate constants of spontaneous cleavage appear to be a little higher than that of dibenzoyl peroxide and are, in increasing sequence: benzoyl < furoyl < bromofuroyl < furylacryloyl peroxide. If, as put forward by Swain et al. (14) for benzoyl peroxide, the most important in-

fluence governing the rate seems to be the magnitude of the coulombic repulsion between the opposing dipoles at the two ends of the molecule



$$\underset{\delta^+\delta^-}{\underrightarrow{R-\overset{\overset{O}{\|}}{C}-O}}-\underset{\delta^-\delta^+}{\underleftarrow{O-\overset{\overset{O}{\|}}{C}-R}}\,,$$

the more rapid spontaneous cleavage of furoyl peroxide can be explained by the prevalent electron-donating character of furane cycle. The high rate of decomposition of furilacryloyl peroxide can be explained not only by the electron-donating character of furane cycle, but, first of all by, the formation of a stable radical of mezomeric structure.

4. The rate constants of induced decomposition appear to be extremely high and increase in the same sequence as k_d.

Summary

The thermal decomposition of di-2-furoyl, di-5-bromo-2-furoyl, di-2-furil-ß-acryloyl peroxides and, for the sake of comparison, dibenzoyl peroxide has been investigated in different types of solvents (benzene, dichloroethane, cyclohexane, dioxan, ethyl acetate, methanol, acetic acid).

The decomposition of the peroxides containing furane cycle seems to be essentially of the same complex nature as that of benzoyl peroxide, but these peroxides seem to be more liable to induced decomposition. The overall rate of decomposition of these peroxides seems to be high. The specific rate constants of spontaneous cleavage appear to be a little higher than that of dibenzoyl peroxide and are in increasing order of: benzoyl $<$ furoyl $<$ bromofuroyl $<$ furilacryloyl peroxide. The rate constants of induced decomposition appear to be extremely high and increase in the same order as k_d.

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