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KINETICS AND MECHANISM OF DIMETHYLCADMIUM AUTO-OXIDATION IN DECANE *

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Summary

The liquid-phase auto-oxidation of dimethylcadmium in n-decane has been investigated at 45—60°C The process occurs by a chain free-radical mechanism, to give the auto-oxidation products MeOOCdMe and $(MeOO)_2Cd$ The chain-initiation reaction has been studied by the inhibitor method The rate of radical generation decreases with increasing oxygen concentration in the reaction mixture The role of peroxide products in the auto-oxidation process has been clarified, and the probable mechanism of dimethylcadmium auto-oxidation is discussed

Results and discussion

Dimethylcadmium auto-oxidation has not previously been studied sufficiently All that was hitherto known was that the process proceeds through a chain free-radical mechanism, and leads to the formation of methyl(methylperoxy)cadmium [1] In the present work, the mechanism of this process is reported in detail

Dimethylcadmium oxidation was conducted in n-decane The temperature of reaction was maintained in the range 45—60°C, the initial dimethylcadmium concentration ranged from 1×10^{-2} to 5×10^{-2} mol/l, and that of oxygen from 3×10^{-3} to 9×10^{-3} mol/l Dimethylcadmium auto-oxidation proceeds in two successive macro-stages, separated in time, with $N \simeq 1$, where N is the number of moles of oxygen consumed per mole of initial OEC (Fig 1). As we reported earlier [2], the product of the first macro-stage is methyl(methylperoxy)cadmium, and that of the second macro-stage is di(methylperoxy)cadmium (peroxides I and II, respectively) The rate of the first macro-stage is about one

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* Dedicated to Professor H Normant in recognition of his contributions to chemistry

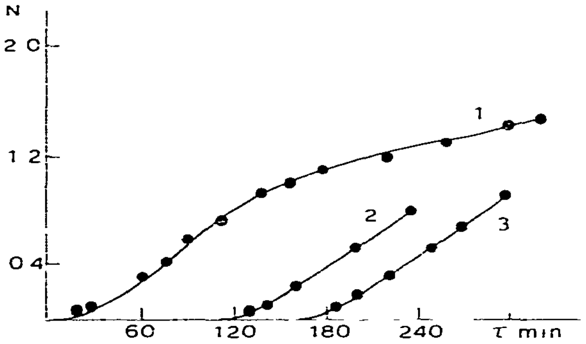


Fig 1 Dimethylcadmium auto-oxidation in n-decane at 30°C (C_0 = 0.064 mol/l [O_2] = 5.6 × 10^{-3} mol/l) 1 Without inhibitor 2 3 in the presence of phenthiazine at concentrations of $C_{0\ \mathrm{InH}} = 3 \times 10^{-5}$ mol/l and 4 × 10^{-5} mol/l respectively

order of magnitude higher than that of the second macro-stage On this assumption, the yields of peroxides I and II should correspond to the stoichiometries of the following, successive macro-stages (1,2)

$$(H_3C)_2Cd + O_2 \rightarrow H_3CCdOOCH_3 \qquad (1)$$

$$H_3CCdOOCH_3 + O_2 \rightarrow Cd(OOCH_3)_2 \qquad (2)$$

The results obtained indicate that, in the course of dimethylcadmium auto-oxidation in n-decane, the transformations of organo-cadmium peroxides which were earlier supposed to take place, i e rearrangement of peroxide (I) in dimethoxycadmium or dimethylcadmium oxidation, either do not take place or do not exert an essential influence upon the composition of the reaction products (3,4).

$$H_3CCdOOCH_3 \rightarrow Cd(OCH_3)_2 \qquad (3)$$

$$H_3CCdOOCH_3 + Cd(CH_3)_2 \rightarrow 2\ H_3CCdOCH_3 \qquad (4)$$

Dimethylcadmium auto-oxidation in the first macro-stage proceeds by first-order kinetics with respect to the initial Me_2Cd concentration. The appearance of the kinetic curves points to the autocatalytic nature of the process (Fig 1).

The maximum rate of the process increases with decreasing concentration of oxygen in the reaction mixture (Fig. 2). The apparent rate constant of the overall process is satisfactorily described by the Arrhenius equation (see Fig 3), with an oxygen concentration of 5.6 × 10^{-3} mol/l it is of the following form·

$$k_{ef} = 10^{9.5} \exp(-19500/RT) \mathrm{l\ mol^{-1}\ sec^{-1}}$$

As mentioned above, the dimethylcadmium auto-oxidation process proceeds by a chain free-radical mechanism. The primary reaction might be supposed to represent the formation of the complex $Me_2Cd \cdot O_2$, by analogy with the case of diethylcadmium auto-oxidation [4]. As a result, the complex transformation leads to radical generation, i.e. chain initiation. However, the chain-initiation mechanism has proved to be different.

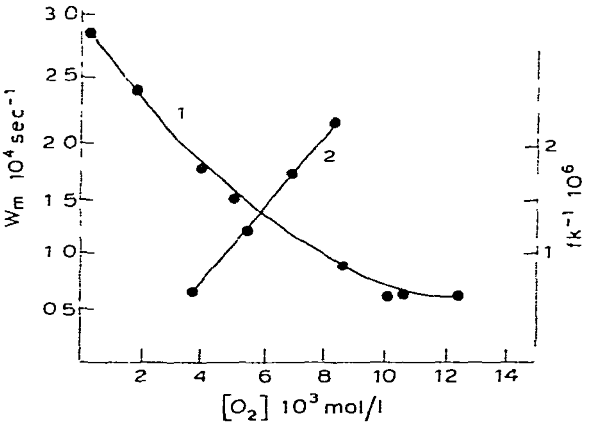


Fig 2 Effect of the concentration of oxygen in the reaction mixture (1) on W_m (W_m is estimated from the maximum slope of the corresponding kinetic curves) and (2) on l for the chain initiation reaction during Me_2Cd auto oxidation in n-decane at 50°C

In dimethylcadmium auto-oxidation, the primary reaction was conducted by the inhibitor method· one of the more effective inhibitors, as measured by induction-appearance period (τ_{ind}), proved to be phenthiazine (Fig 1) τ_{ind} increases linearly with initial phenthiazine concentration ($[InH]_0$ from $0\ 5 \times 10^{-5}$ to 5×10^{-5} mol/l) (Fig 4), and consumption of phenthiazine during the induction period occurs at a constant rate (Fig. 5) Therefore [5], an ordinary relation exists between the chain initiation rate (W_0), $[InH]_0$, and τ_{ind} (namely, $W_0 = f[InH]_0/\tau_{ind}$, where f = inhibition ratio on phenthiazine).

Investigation of the influence of various kinetic factors upon the quantity τ_{ind} showed that the chain initiation proceeds via a second-order reaction relative to dimethylcadmium (Fig 6), and that the reaction order relative to oxygen is negative (Fig 2) The rate constant of chain initiation (k) is satisfactorily

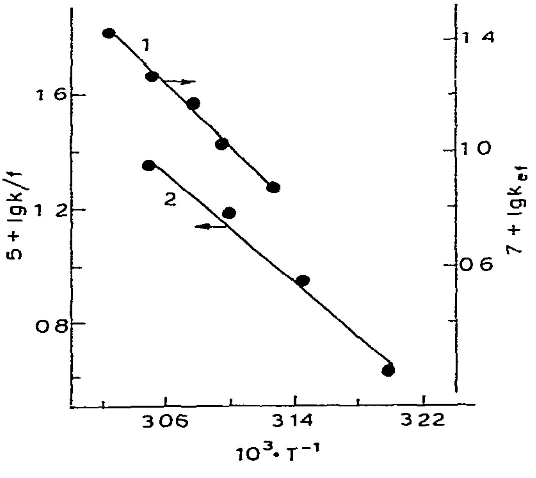
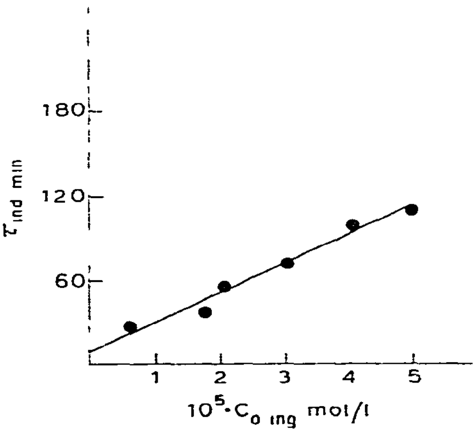


Fig 3 Dimethylcadmium auto-oxidation in n-decane (C_0 = 0 04 mol/l, $[O_2] = 5\ 6 \times 10^{-3}$ mol/l) Temperature dependence of k_{eff} for the total process and of k for the chain-initiation reaction (curves 1 and 2 respectively)



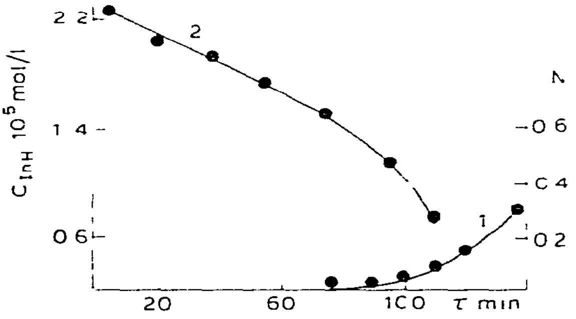


Fig 4 Dimethylcadmium auto-oxidation in n-decane (C_0 = 0 03 mol/l $[O_2]$ = 5 6 $\times 10^{-3}$ mol/l at 30 C) The effect of the initial concentration of phenthiazine on τ_{ind}

Fig 5 Dimethylcadmium auto-oxidation in n-decane at 50°C (C_0 = 0 064 mol/l $[O_2]$ = 5 6 $\times$ 10^{-3} mol/l) 1, In the presence of phenthiazine ($C_{0,InH}$ = 2 3 $\times 10^{-5}$ mol/l) 2 consumption of phenthiazine in the induction period

described by the Arrhenius equation (see Fig. 3), with an oxygen concentration of 5.6 $\times 10^{-3}$ mol/l, it is of the form

$$k = 10^{10} \exp(-23500/RT) \quad f \, l \, mol^{-1} \, sec^{-1}$$

At 50° C, and with the oxygen concentration $[O_2]$ within the limits of the above-mentioned range, the quantity k decreases with increasing oxygen concentration, in accordance with the equation $f \ (k)^{-1} = -0\ 553 \times 10^6 + 0\ 33 \times 10^9 \cdot [O_2]$. The investigation shows that the chain initiation in the dimethylcadmium auto-oxidation process is a result of two dimethylcadmium molecules interacting via a bimolecular mechanism It is known [6] that the kinetic char-

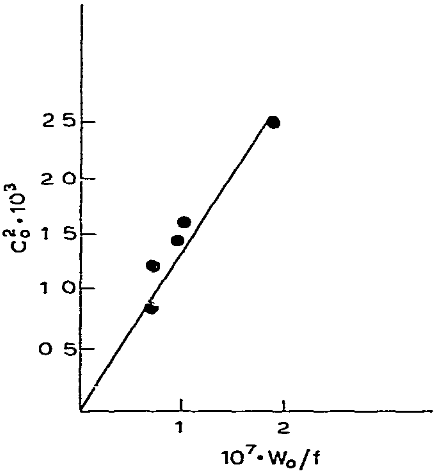
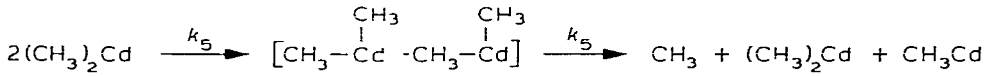
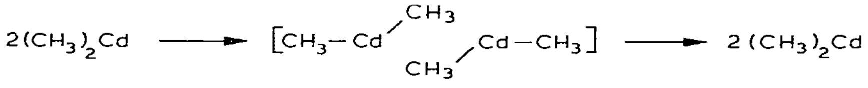


Fig. 6. Effect of the initial concentration of dimethylcadmium on the chain initiation rate at 50° C ($[InH]_0$ = 1 5 $\times 10^{-5}$ mol/l, $[O_2]$ = 5 6 $\times 10^{-3}$ mol/l)

acteristics of homo-exchange reactions of the second-group-element organic compounds, proceeding via the formation of an intermediate cyclic complex, are analogous It is believed that the chain initiation and the homo-exchange represent concurrent reactions, proceeding with the formation of complexes of noncyclic and cyclic types, respectively

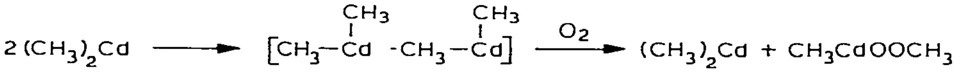


$$2(CH_3)_2Cd \xrightarrow{k_5} [CH_3-\overset{CH_3}{\overset{|}{Cd}}-CH_3-\overset{CH_3}{\overset{|}{Cd}}] \xrightarrow{k_5} CH_3 + (CH_3)_2Cd + CH_3Cd \tag{5}$$



$$2(CH_3)_2Cd \longrightarrow [CH_3-Cd\genfrac{}{}{0pt}{}{\diagup CH_3}{CH_3\diagup}Cd-CH_3] \longrightarrow 2(CH_3)_2Cd \tag{6}$$

The following reaction is also competitive with reaction 5



$$2(CH_3)_2Cd \longrightarrow [CH_3-\overset{CH_3}{\overset{|}{Cd}}-CH_3-\overset{CH_3}{\overset{|}{Cd}}] \xrightarrow{O_2} (CH_3)_2Cd + CH_3CdOOCH_3 \tag{7}$$

The competition of reactions 5 and 7 gives rise to the above-mentioned negative reaction order of the chain initiation relative to oxygen

A large amount of methyl(methylperoxy)cadmium, introduced into the reaction mixture before beginning dimethylcadmium oxidation, decreases to some extent the induction period of the process (Fig 7) However, the peroxide consumption is not appreciable It should be also noted that the thermal decomposition of organo-cadmium peroxides in hydrocarbons proceeds at a considerable rate at temperatures above 60°C [7] The influence of methyl(methylperoxy) cadmium upon the rate of dimethylcadmium auto-oxidation is indicative of the participation of this peroxide in the generated chain branching reaction The nature of this reaction is of particular interest

Cadmium alkyl derivatives, as well as those of other elements of the second group, are known to react readily in exchange reactions with salt-like compounds

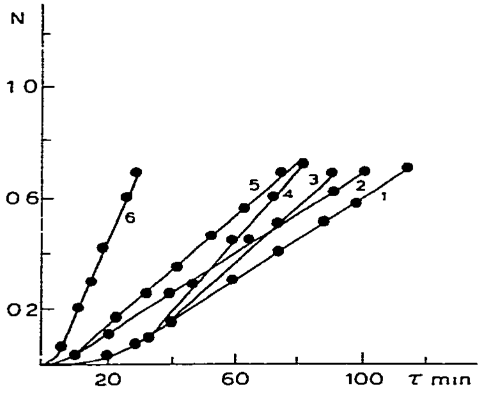


Fig. 7 Dimethylcadmium auto-oxidation in n-decane at 50°C (C_0 = 0 03 mol/l, [O_2] = 5 6 × 10^{-3} mol/l) 1 Without additions and with the following additions (mol%) 2 MeOOCdMe(30) 3 TGF(10) 4 pyridine(10) 5, $CdCl_2$(1000) 6, MeOCdMe(1000)

TABLE 1

COMPOSITION OF THE GASEOUS MIXTURE PRODUCED BY THE INTERACTION BETWEEN $CdCl_2$ AND $(CH_3)_2Cd$ [a] IN n-DECANE

c_0 $(CH_3)_2Cd$ 0 03 mol/l T_{react} 20°C reaction time 2 h

	CH_4	CH_3Cl	Unsaturated hydrocarbons C_3—C_6	Saturated hydrocarbons	Alcohols	Non-identified products
Volume (%)	81 7	0 65	3 2	5 4	0 5	9

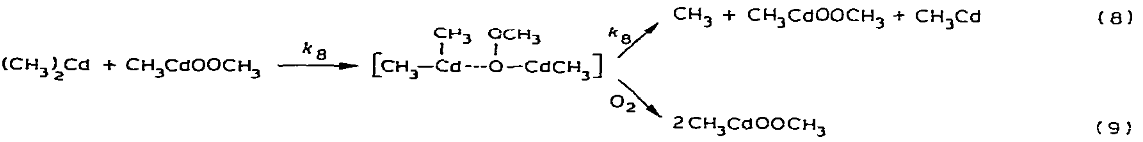
[a] MeOCdMe undergoes an analogous reaction (Fig 7)

of the same elements [6,8] We investigated the products of such a reaction, using as an example the interaction between Me_2Cd and $CdCl_2$ in n-decane, which proceeds well even at room temperature The main gaseous product of this reaction was methane (Table 1), which points to methyl-radical formation as a result of interaction between Me_2Cd and $CdCl_2$. Consequently, the concurrent reactions also occur in this case, leading to exchange product formation and generation of radicals [reactions of types (5) and (6)] In accordance with these results, the addition of cadmium halogen derivatives to Me_2Cd accelerates substantially its oxidation reaction (Fig 7), and the quantity of oxygen absorbed (per mole of Me_2Cd) decreases as the amount of CdX_2 introduced increases, because substitution by the halogen of the methyl radical at Cd the atom competes efficiently with the oxidation reaction

It should be noted that in the above-mentioned chain-initiation reactions, the intermediate complexes of non-cyclic type can be considered as Me_2Cd, specifically solvated by the ligand (which may be the second molecule of Me_2Cd, $CdCl_2$, MeCdOMe, and so on). The positive kinetics effect of OEC solvation by electron donors in oxidation reactions employing oxygen has been investigated earlier for a number of related compounds. Analogous results have been obtained in the present work. The auto-oxidation of Me_2Cd is effectively accelerated by the addition of pyridine and tetrahydrofuran (Fig 7), which specifically solvate the initial CdOC and undergo no changes in the process

It should be noted that the auto-oxidation of Me_2Cd in the presence of CdX_2, MeCdOMe, pyridine and tetrahydrofuran is not accompanied by consumption of methyl(methylperoxy)cadmium.

By analogy with reactions (5) and (7), the following modes of chain branching involving MeCdOOMe probably occur (8, 9).



$$(CH_3)_2Cd + CH_3CdOOCH_3 \xrightarrow{k_8} [CH_3-\overset{CH_3}{\overset{|}{Cd}}\cdots\overset{OCH_3}{\overset{|}{O}}-CdCH_3] \xrightarrow{k_8} CH_3 + CH_3CdOOCH_3 + CH_3Cd \quad (8)$$

$$[CH_3-\overset{CH_3}{\overset{|}{Cd}}\cdots\overset{OCH_3}{\overset{|}{O}}-CdCH_3] \xrightarrow{O_2} 2CH_3CdOOCH_3 \quad (9)$$

Other possible chain-branching pathways are not likely to be significant This is because the rate of chain branching is at a maximum when the concentrations of Me_2Cd and MeCdOOMe are comparable, i.e. when the degree of auto-oxidation, N, is about 0.5 (Fig. 8).

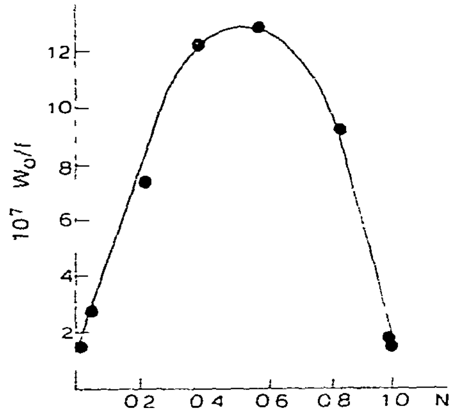


Fig 8 Change of radical generation rate during dimethylcadmium oxidation in n-decane at 50°C (C_0 = 0 044 mol/l $[O_2]$ = 5 6 × 10^{-3} mol/l and $C_{0\ \mathrm{InH}}$ = 3 7 × 10^{-4} mol/l)

The results of the investigation suggest the following chain-propagation reactions (10—11)

$$^\bullet CH_3 + O_2 \rightarrow H_3CO_2^\bullet \qquad (10)$$

$$H_3CO_2^\bullet + (CH_3)_2Cd \rightarrow CH_3CdOOCH_3 + {}^\bullet CH_3 \qquad (11)$$

and the chain termination reaction

$$CH_3O_2^\bullet + CH_3O_2^\bullet \rightarrow \text{products} \qquad (12)$$

According to the reaction scheme, the rate of auto-oxidation appears to be as follows

$$W = \frac{k_{11}}{\sqrt{k_{12}}} \cdot [(CH_3)_2Cd] \times \sqrt{\frac{k'_5 k''_5 [(CH_3)_2Cd]^2}{k''_5 + k_7[O_2]} + \frac{k'_8 \quad k''_8 [(CH_3)_2Cd]([(CH_3)_2Cd]_0 - [(CH_3)_2Cd])}{k''_8 + k_9[O_2]}}$$

In the initial stage

$$W = k'_{\mathrm{ef}}[(CH_3)_2Cd]^2$$

where

$$k'_{\mathrm{ef}} = \frac{k_{11}}{\sqrt{k_{12}}} \sqrt{\frac{k'_5 k''_5}{k''_5 + k_7[O_2]}}$$

As the process develops

$$W = k''_{\mathrm{ef}}[(CH_3)_2Cd]\sqrt{[(CH_3)_2Cd][CH_3OOCdCH_3]}$$

where

$$k''_{\mathrm{ef}} = \frac{k_{11}}{\sqrt{k_{12}}} \sqrt{\frac{k'_8 k''_8}{k''_8 + k_9[O_2]}}$$

The scheme of dimethylcadmium auto-oxidation given above does not involve the abstraction of hydrogen from the solvent and organoelement compounds by $RO_2^{\bullet}$ radicals. This is because, at a coordinatively-unsaturated atom of the metal (for example Cd), homolytic substitutions by peroxy radical proceed readily For example, on auto-oxidation of boron alkyls, the rate constant of the reaction of substitution by n-butylperoxy radical in tri-n-butylboron is found to be 10^7 times higher for the boron atom than it is for benzyl hydrogen in a similar reaction in toluene (this reaction is usually considered to be a process of hydrogen-atom abstraction) [9]

Experimental

Dimethylcadmium was prepared by a known procedure [8] The purification of the compound (three-fold re-condensation) and preparation of its solutions were performed under vacuum. Me_2Cd oxidation was carried out in sealed glass apparatus. Continuous mixing with a magnetic stirrer provided complete saturation of the reaction mixture with oxygen $(CH_3)_2Cd$ auto-oxidation was tested for oxygen absorption The concentrations of dimethylcadmium stock solutions were estimated iodometrically under vacuum [10]

Methyl(peroxymethyl)cadmium

A solution of Me_2Cd was oxidized ($N = 1$), the solvent was evaporated, and a white crystalline solid precipitate of low solubility in n-hydrocarbons was obtained Aliquots of the peroxide were hydrolyzed under vacuum, and the compounds formed were analysed. CH_4 evolved was estimated volumetrically and mass-spectrometrically MeOOH was identified and determined quantitatively by gas-liquid chromatography on a "Tsvet-102" chromatograph, a glass column ($l = 2$ m), packed with 15% PEG-400 on Chromaton N-AWDMCS, was used ($T_{evap} = T_{det} = 80°C$, $T_{col} = 60°C$, detector bridge current = 200 ma, $V_{He} = 35$ ml/min). Peroxidic oxygen was analysed iodometrically [11], and Cd^{2+} complexometrically [12]. The peroxide structure suggested was confirmed by IR spectra, which were recorded using a UR-20 apparatus. Me_2Cd spectra were recorded using solutions in n-decane, placed in a vacuum cuvette. Other samples were prepared in an inert atmosphere as suspensions in vaseline oil

Di(methylperoxy)cadmium, prepared by oxidation of dimethyl-cadmium solution ($N = 2$), is a white crystalline precipitate, practically insoluble in aprotic solvents. The peroxide structure was confirmed by the same method used in the case of MeOOCdMe.

Consumption of the inhibitor (phenthiazine) was monitored by using a "Tsvet-304" gas-liquid chromatograph with a UV detector (eluent = decane + 1 5% TGF, $l = 20$ cm, stationary phase = Silochrom). The process was interrupted at the required moment, the reaction mixture was degassed and hydrolyzed, and the sample was injected into the chromatograph

Reaction between $CdMe_2$ and $CdCl_2$

Me_2Cd in n-decane solution was added under vacuum to a 30-fold excess of $CdCl_2$ heated to 150°C. Bubbles of gas were observed to evolve The mixture was allowed to stand for 2 h at room temperature. Some 2% of CH_4 was evolved (relative to the total initial methyl groups in Me_2Cd).

Isomolar concentration method

Constant aliquots of phenthiazine were introduced into the reaction mixture at $1 \geqslant N \geqslant 0$ Radical generation rate was estimated from the dependence of τ_{ind} on the time of inhibitor introduction

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