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# NUCLEOPHILIC CHARACTER OF ALKYL RADICALS—VIII[1]

## KINETICS AND MECHANISM OF INDUCED DECOMPOSITION OF DECANOYL PEROXIDE IN THE HOMOLYTIC ALKYLATION OF PROTONATED QUINOLINE

F. MINISCI and A. SELVA
Istituto di Chimica del Politecnico, Prazza L. da Vinci 32, 20133 Milano, Italy

and

O. PORTA, P. BARILLI and G. P. GARDINI
Istituto di Chimica Organica dell'Università, Via M. D'Azeglio 85, 43100 Parma, Italy

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**Abstract**—The thermal decomposition of decanoyl peroxide in benzene, heptane, quinoline, acetic acid and quinoline in acetic acid was studied. Kinetics and reaction products in the first four solvents follow the usual pattern of the acyl peroxides decomposition. However, in the presence of protonated quinoline a remarkable example of induced decomposition was found. First-order kinetics in peroxide indicates that a cross-termination is operative in a radical chain. The composition of the reaction products is also highly simplified in comparison with that obtained in the other solvents: only 2- and 4-nonylquinolines, decanoic acid and traces of octadecane are formed. Kinetics and reaction products are discussed in terms of a free-radical chain mechanism, in which the nucleophilic character of the nonyl radical plays an important role.

## INTRODUCTION

THE homolytic alkylation of protonated heteroaromatic bases has a theoretical and synthetic interest comparable to the electrophilic alkylation in the homocyclic series.[1,2] Unprotonated heteroaromatic bases and homocyclic aromatic substrata show quite different behaviour and homolytic alkylation has a very poor synthetic interest owing to many side reactions and low selectivity. This substantially different behaviour was interpreted in terms of the transition state, which would be more similar to a $\sigma$-complex with homocyclic and unprotonated heteroaromatic substrata and more similar to a $\pi$-complex with protonated heteroaromatic substrata.[1] In this last case the polar characteristics of both the alkyl radical and the aromatic substratum are highly prevalent over the stability of the intermediate radicals, which obviously plays a primary role in a transition state similar to a $\sigma$-complex. The same trend was not observed in the homolytic arylation of protonated heteroaromatic bases owing to the poor polar character of the aryl radicals.

Now we report that the thermal decomposition of decanoyl peroxide in the presence of quinoline and other protonated heteroaromatic bases gives rise to one of the most remarkable cases of induced decomposition till now observed with this kind of peroxide in aromatic solvents. The results strongly support our previous conclusions,[1] obtained from the study of the substituent effect, concerning the influence of the nucleophilic character of the alkyl radicals in the homolytic alkylation of protonated heteroaromatic bases.

## RESULTS AND DISCUSSION

The dramatic change in selectivity in the homolytic aromatic alkylation observed by merely protonating the heteroaromatic bases induced us to study in the presence of these bases the kinetics of peroxide decomposition, which give rise to alkyl radicals.

It is well known that the rate of the radical decomposition of peroxides is generally determined by the homolytic scission of the peroxide bond:

$$\mathrm{R{-}O{-}O{-}R \rightarrow 2\,R{-}O\cdot}$$

Solvents do not much affect the rate of this scission, unless radicals arising from the solvent give rise to induced decomposition.

In this work we report the decomposition kinetics of decanoyl and benzoyl peroxides in quinoline acetic acid solutions and in solutions of unprotonated quinoline, benzene, heptane and acetic acid. Furthermore by means of the competitive method we have tried also to determine the rates (relative to benzene) at which quinoline, protonated or not, is alkylated by the nonyl radical arising from the decomposition of decanoyl peroxide. The study of the reaction products by combined gas-chromatography and mass spectrometry (GLC–MS) together with kinetic data supplied a satisfactory picture of the reaction mechanism.

*Reactions products. Decanoyl peroxide in heptane.* The composition of the reaction products is very complex as shown by the chromatogram in Fig 1. The analysis was carried out by GLC–MS and the results are summarized in Table 1. These percentages are only based on the areas of the peaks of the isomer mixtures since it is very difficult to separate the single isomers. The formation of the reaction products can be explained by the following scheme:

$$\mathrm{R{-}COOOCO{-}R \rightarrow 2\,R{-}COO\cdot} \qquad \mathrm{R = n\text{-}C_9H_{19}}$$
$$\mathrm{R{-}COO\cdot \rightarrow R\cdot + CO_2} \qquad \mathrm{R' = C_7H_{15}}$$
$$\mathrm{R\cdot + R'{-}H \rightarrow R{-}H + R'\cdot} \qquad \mathrm{R'' = n\text{-}C_4H_9{-}CH{-}C_4H_9\text{-}n}$$
$$\mathrm{R{-}COO\cdot + R'{-}H \rightarrow R{-}COOH + R'\cdot}$$
$$\mathrm{R\cdot \rightarrow R''\cdot}$$
$$\mathrm{R\cdot + R\cdot \rightarrow R{-}R}$$
$$\mathrm{R\cdot + R\cdot \rightarrow R{-}H + R_{(-H)}}$$
$$\mathrm{R\cdot + R'\cdot \rightarrow R{-}R'}$$
$$\mathrm{R\cdot + R''\cdot \rightarrow R{-}R''}$$
$$\mathrm{R'\cdot + R'\cdot \rightarrow R'{-}R'}$$
$$\mathrm{R\cdot + R{-}COO\cdot \rightarrow R{-}COOR}$$
$$\mathrm{R\cdot + R{-}COO\cdot \rightarrow R_{(-H)} + R{-}COOH}$$

TABLE 1. DECOMPOSITION PRODUCTS OF DECANOYL PEROXIDE IN HEPTANE (mol %)

| nonane + nonene-1% | $C^{14}$ alkanes% | $C^{16}$ alkanes% | octadecane% | isooctadecane% | nonyl decanoate% | decanoic acid% |
|---|---|---|---|---|---|---|
| 53·8 | 4·0 | 4·1 | 18·6 | 0·6 | 10·6 | 8·3 |

It is interesting to point out that of the ten isomers which can be obtained by combination of $C_7H_{15}$ radicals, six were characterized as $C_{14}$ hydrocarbons and of the four possible isomers obtainable from cross-combination of n–$C_9H_{19}$ and $C_7H_{15}$ radicals, three were characterized as $C_{16}$ hydrocarbons The almost identical percentages of $C_{14}$ and $C_{16}$ alkanes would indicate that the steady concentration of nonyl radicals, which escape from the cage, and heptyl radicals arising from the solvent are of the same order of magnitude.

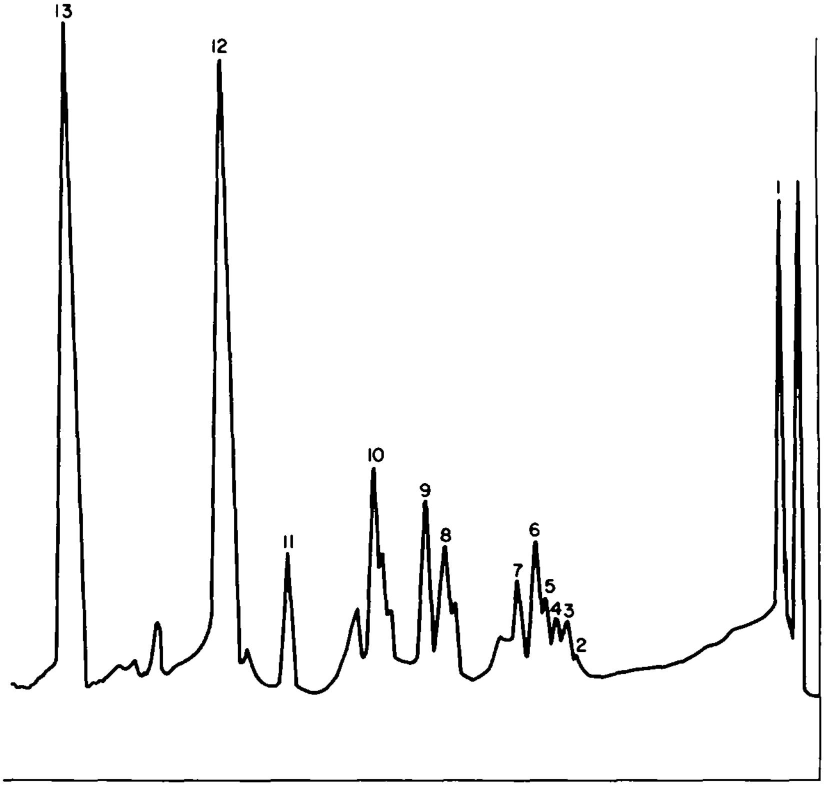


FIG 1. Chromatogram of the decomposition products of decanoyl peroxide in heptane. 1: nonane + nonene-1; 2,3,4,5,6 and 7: $C_{14}$ alkanes; 8,9 and 10: $C_{16}$ alkanes; 11: iso-octadecane; 12: octadecane; 13: nonyl decanoate

The structure of the radical R″• was assumed on the grounds of the results obtained in benzene. Its formation would be due to an intramolecular hydrogen abstraction, which has been generally accepted as the basis for the formation of butyl-chain branches in polyethylene.

*Decanoyl peroxide in benzene.* In addition to nonane, nonene-1, octadecane and nonyl decanoate, products of attack of the nonyl radical to the solvent are also formed. The acidic products and the involatile residue were not examined. The results are shown in Table 2. GLC–MS (Fig 5) allowed us to characterize (besides n-nonylbenzene) the branched isomer $C_6H_5CH(CH_2—CH_2—CH_2—CH_3)_2$. This

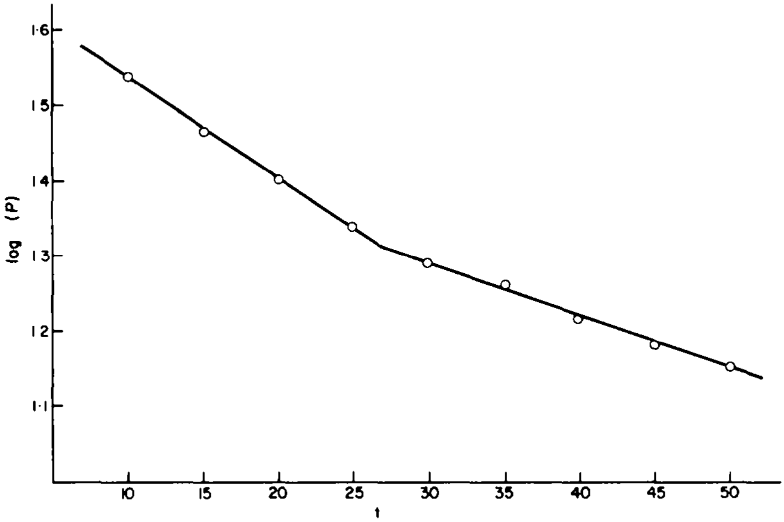


FIG 2. Kinetics of the decomposition of 0·2 mol decanoyl peroxide in acetic acid at 70° (run 4 of Table 6)

fact represents an interesting experimental verification of intramolecular hydrogen abstraction in long alkyl radicals which occurs in the polymerization of ethylene, thus supporting the structure assumed for isooctadecane and furthermore it is an

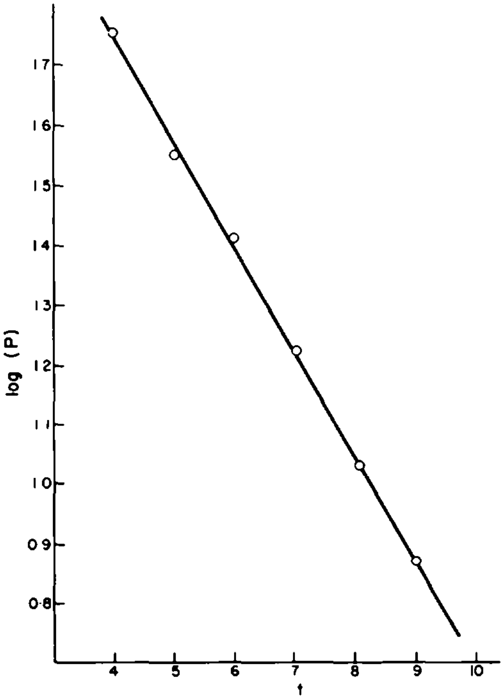


FIG 3. Kinetics of the decomposition of 0·2 mol decanoyl peroxide in acetic acid at 70° (run 10 of Table 6)

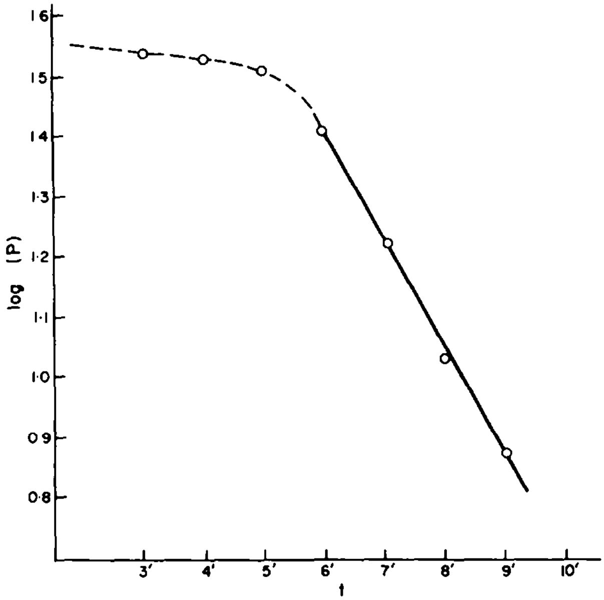
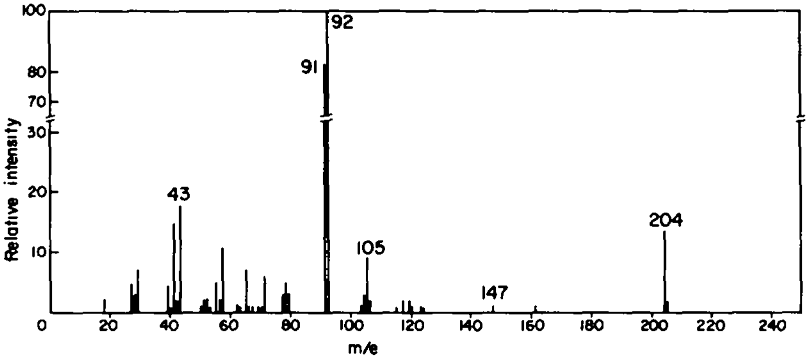


Fig 4. Kinetics of the decomposition of 0·2 mol decanoyl peroxide in acetic acid at 70° (run 10 of Table 6) in the presence of traces of 2,4,6-tri-t-butylphenol



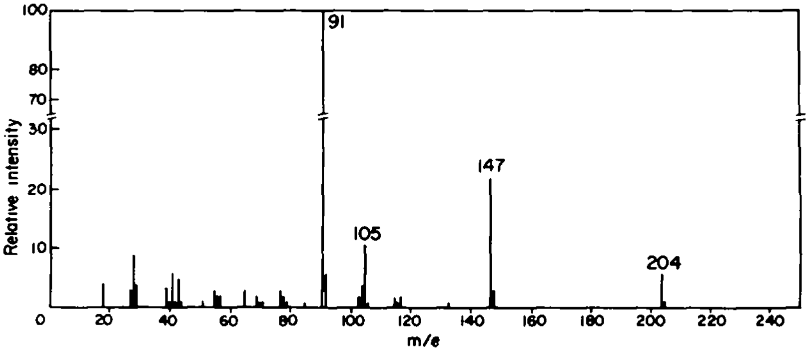


Fig 5a. Mass spectrum of 1-phenylnonane
Fig 5b. Mass spectrum of 5-phenylnonane

interesting case of homolytic aromatic alkylation, in which the alkyl radical isomerizes before attacking the aromatic ring.

TABLE 2. DECOMPOSITION PRODUCTS OF DECANOYL PEROXIDE IN BENZENE (mol %)

| nonane + nonene-1% | isononylbenzene% | nonylbenzene% | octadecane% | nonyl decanoate% | *o*, *m* and *p* dinonylbenzene% |
|---|---|---|---|---|---|
| 52·8 | 0·2 | 11·3 | 23·8 | 11·4 | 0·5 |

*Decanoyl peroxide in acetic acid.* The main decomposition products are still nonane, nonene-1, octadecane and nonyl decanoate. The relative percentages are shown in Table 3. The acidic products were not examined.

*Decanoyl peroxide in acetic acid and quinoline.* In the presence of an excess of quinoline only four products are formed: octadecane (1·3% mole/mole peroxide), 2- and 4-nonylquinolines (97–98% mole/mole peroxide) and decanoic acid (almost one mole for mole of peroxide). Only a small percentage of the nonyl radicals do not attack quinoline; neither is a remarkable amount of involatile residue formed. The structure of the two nonylquinolines was assumed on the grounds of the results obtained with valeroyl peroxide under the same experimental conditions: only the known 2- and 4-butylquinolines were formed.

TABLE 3. DECOMPOSITION PRODUCTS OF DECANOYL PEROXIDE IN ACETIC ACID (mol %)

| nonane + nonene-1% | octadecane % | nonyl decanoate % |
|---|---|---|
| 67·0 | 24·6 | 8·4 |

In the presence of a small amount of quinoline, 2,4-dinonylquinoline and considerable amounts of nonane, nonene-1, octadecane and nonyl decanoate are formed. The ratios of the nonyl radicals, which attack the quinoline or dimerize to octadecane with the change of quinoline concentration are shown in Table 4.

TABLE 4. RATIOS OF OCTADECANE AND NONYLQUINOLINES (mol %) IN THE DECOMPOSITION OF DECANOYL PEROXIDE IN ACETIC ACID

| Run | Molar ratio quinoline:peroxide | octadecane% | nonylquinolines*% |
|---|---|---|---|
| 2 | 0·1 | 38·7 | 61·3 |
| 3 | 0·2 | 26·2 | 73·8 |
| 4 | 0·4 | 12·7 | 87·3 |
| 6 | 0·8 | 3·9 | 96·1 |
| 7 | 1·6 | 2·6 | 97·4 |
| 8 | 3·2 | 2·0 | 98·0 |
| 9 | 6·4 | 1·7 | 98·3 |
| 10 | 12·8 | 1·3 | 98·7 |

* 2- and 4-nonylquinolines are present and, at low quinoline concentrations, also 2,4-dinonylquinoline is formed; the mol% of 2,4-dinonylquinoline was doubled

Isononylquinoline was not observed; the great affinity of the nonyl radical towards the protonated quinoline prevents the radical from isomerising before attacking the heteromatic ring.

*Decanoyl peroxide in quinoline.* The reaction products are quite different from those obtained in the presence of protonated quinoline. The percentage of nonyl radicals which attack quinoline is much lower; considerable amounts of nonane, nonene-1, octadecane, nonyl decanoate and involatile residue are formed (Table 5).

TABLE 5. DECOMPOSITION PRODUCTS OF DECANOYL PEROXIDE IN QUINOLINE (mol %)

| nonane + nonene-1% | octadecane% | nonyl-decanoate% | nonylquinolines% |
|---|---|---|---|
| 21·0 | 16·9 | 5·2 | 56·6 |

Attack of the nonyl radical on quinoline is not selective; five nonylquinoline isomers were identified by GLC-MS and probably the other three isomers are also present (the separation by GLC is rather difficult since superposition of the isomer peaks takes place).

*Kinetics.* The decomposition rates of decanoyl peroxide in the presence of AcOH and increasing amounts of quinoline are shown in Table 6. At low quinoline concentrations the kinetic course is shown in Fig 2; in these cases the first-order rate constants were calculated from the initial slopes of the graphs and correspond to the presence of quinolines, which have the 2 and 4 positions still free; at the end of the reaction quinoline is transformed into 2,4-dinonylquinoline. At high quinoline concentration a great increase of reaction rate occurs and both the kinetic course and the composition of the products are simplified. The decomposition rate is first-order in peroxide for more than 90% of the reaction (Fig 3) and the nonyl radicals are almost completely trapped by quinoline. The rate constants do not change with changing concentration of decanoyl peroxide. The nature of the reaction products

TABLE 6. FIRST-ORDER RATE CONSTANTS OF DECOMPOSITION OF DECANOYL PEROXIDE (0·2 mol) IN ACETIC ACID IN THE PRESENCE OF QUINOLINE AT 70°

| Run | Molar ratio quinoline : peroxide | $10^5 k$ sec$^{-1}$ |
|---|---|---|
| 1 | 0 | 8·4 |
| 2 | 0·1 | 15·2 |
| 3 | 0·2 | 29·3 |
| 4 | 0·4 | 48·7 |
| 5* | 0·4 | 130·0* |
| 6 | 0·8 | 126·1 |
| 7 | 1·6 | 147·0 |
| 8 | 3·2 | 256·0 |
| 9 | 6·4 | 575·0 |
| 10 | 12·8 | 746·0 |

* In the presence of one mol of TFA for each mol of quinoline

make it unlikely that the large increase of the decomposition rate could be ascribed to a heterolytic scission of the acyl peroxide by the unprotonated quinoline present in acetic acid according to the well known reaction of benzoyl peroxide with aromatic amines[3]:

$$R_3N + RCOOOCOR \rightarrow R_3\overset{+}{N}OCOR + RCOO^-$$

However, the decomposition rate in unprotonated quinoline certainly excludes such a process, because the reaction rate is not much higher than that observed in acetic acid, benzene and heptane and it is much lower than the rate observed in quinoline and acetic acid (Table 7). It is likely that the increase of the decomposition rate in unprotonated quinoline (in comparison with the rate in benzene, acetic acid and heptane) is in part due to the quinoline protonated by decanoic acid formed during the reaction. The influence of protonation of quinoline on the reaction rates is clearly shown by runs 4 and 5 of Table 6. With the same quinoline/peroxide ratio, in the presence of one mole of trifluoroacetic acid per mole of quinoline, kinetics always follows the course indicated in Fig 2, but the rate is considerably increased with higher amount of protonated quinoline. It is interesting to point out that the increase of the rate in run 5 takes place only in the initial period of the reaction, when the protonated quinoline has the 2 and 4 positions still free; in the last part of the reaction, when the 2 and 4 positions of the quinoline are alkylated, the reaction rates are identical in runs 4 and 5.

TABLE 7. HALF LIFES OF 0·2 MOL SOLUTIONS OF DECANOYL PEROXIDE AT 70° (in min.)

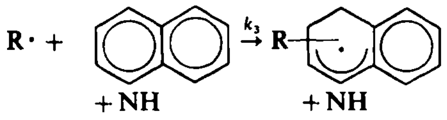
| heptane | benzene | acetic acid | quinoline | quinoline* and acetic acid |
|---|---|---|---|---|
| 492′ | 260′ | 137′ | 68′ 20″ | 1′ 36″ |

* Molar ratio quinoline: peroxide 12·8

The kinetic course and the formation of the reaction products are explained by the following radical chain:

$$RCOOOCOR \xrightarrow{k_1} 2\,RCOO\cdot \qquad (1)$$

$$RCOO\cdot \xrightarrow{k_2} R\cdot + CO_2 \qquad (2)$$



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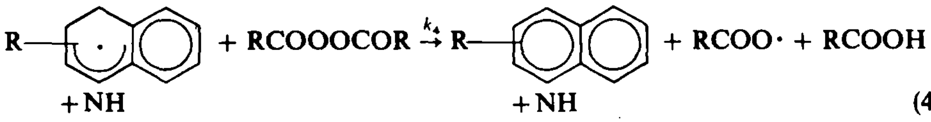
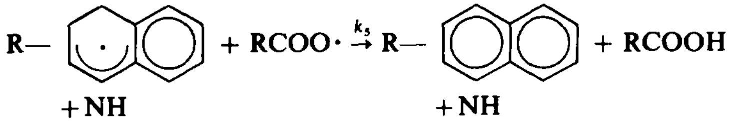


(4)

Decanoyl peroxide is decomposed by thermal homolysis of the peroxide bond (reaction (1)) and by induced decomposition (reaction (4)). In the absence of inhibitors the steady state assumption leads to first order kinetics in peroxide only if a cross-termination takes place according to the following reaction[4]:



(5)

The derived rate law would be:

$$-\frac{d[P]}{dt} = k_1[P] + k_i[P]$$

$$k_i = \tfrac{1}{2}\{-k_1 + k_1^{\frac{1}{2}}k_5^{-\frac{1}{2}}[k_1k_5 + 4k_4(k_2 + k_3)]^{\frac{1}{2}}\}$$

The very small amount of octadecane formed in the presence of protonated quinoline must be ascribed to a cage combination of nonyl radicals arising from reactions (1) and (2). By using commercial decanoyl peroxide with traces of inhibitor (2,4,6-tri-t-butylphenol) an induction period was observed as shown in Fig 4; after this period the reaction proceeds according to the same first-order rate constants observed with purified peroxide. At the same time much higher amounts of octadecane, nonane, nonene-1 and nonyl decanoate were formed. The analysis of the reaction products during the induction period showed that these products were mainly formed during this period; they must be considered arising only from combination and disproportionation of the radicals within the solvent "cage".

The results shown in Table 4 indicate that quinoline and in general protonated heteroaromatic bases (for example pyridine and quinoxaline show analogous behaviour) are among the most effective traps of alkyl radicals. They also indicate that among the causes which determine such a large induced decomposition in the presence of protonated quinoline and not in the presence of unprotonated quinoline, benzene, acetic acid and heptane, the nucleophilic character of the alkyl radical plays a very important role. It determines a very high affinity towards the protonated quinoline and therefore a higher rate in the initiation step (reaction (3)) and a higher kinetic chain length in respect to the other solvents. This is shown by the fact that all the nonyl radicals escaping from the cage are trapped by the protonated quinoline; on the contrary in the other solvents considerable amounts of nonane, always prevailing over nonene-1, cannot arise only from disproportionation of the nonyl radical within the solvent cage, but also from hydrogen abstraction outside the cage. The complete selectivity of attack of the nonyl radical in the 2 and 4 positions of the protonated quinoline and the decrease of the induced decomposition when these positions are substituted (Fig 2) are also significant evidences about the importance of the nucleophilic character of the alkyl radicals in determining the rate of the initiation step of the chain. Further support was obtained from competitive alkylations of benzene and protonated or unprotonated quinoline by the nonyl radical. The unprotonated base is 60 times more reactive than benzene: this value is in good agreement with the value 63 reported by Smid and Szwarc[5] for the ethyl radical. With protonated quinoline, even using a 5:1 benzene/quinoline ratio, only negligible traces (<0·5%) of nonyl benzene were observed by GLC; these do not allow a quantitative determination of the relative rate but certainly indicate that a very high increase of the affinity of the nonyl radical towards the base took place.

As regards the kinetic chain length we can also assume in the termination step (reaction (5)) that protonation of the $\sigma$-complex (I) does not favour the process owing to the electrophilic character of the acyloxy radical; therefore the kinetic chain length should increase in comparison to a termination step involving unprotonated quinoline.

It is interesting to point out that increase of decomposition rate of acyl peroxides with cuprous salts by addition of heteroaromatic bases in acetic acid was already observed by Kochi *et al.*[6] It was ascribed to the ligand nature of the base with regard to the copper salts. Our results would indicate that, at least in part, the catalytic course could be ascribed to a decomposition of the acyl peroxide induced by the protonated base. This view is supported also by the fact that, working under the same conditions used by Kochi in the presence of one mole of quinoline for each mole of isovaleroyl peroxide, 70% of quinoline was transformed in 2- and 4-isobutylquinoline and 2,4-diisobutylquinoline. That is attack at the protonated base successfully competes with oxidation of the alkyl radical by cupric salt, which is the sole reaction in the absence of quinoline:

$$C_4H_9\cdot + Cu^{++} \rightarrow C_4H_8 + Cu^{+} + H^{+}$$

We observed a quite different course with benzoyl peroxide. The increase of decomposition rate on going from unprotonated to protonated quinoline is relatively small. In Table 8 the decomposition rates of benzoyl and decanoyl peroxides in quinoline, acetic acid and solutions of quinoline in acetic acid, are compared. The rates are indicated as half lives in place of the first-order constants because the results with benzoyl peroxide immediately show the absence of the induced decomposition of the same extent observed with decanoyl peroxide and therefore a complete study to determine the kinetic order was not carried out with benzoyl peroxide. In this case generally the order of the induced step in peroxide is 1·5 in aromatic solvents[7] indicating that the chains are terminated by dimerization or disproportionation involving like radicals.

Table 8. Half lifes of 0·2 mol solutions of decanoyl and benzoyl peroxides at 70° (in min.)

| | quinoline | acetic acid | quinoline* and acetic acid |
|---|---|---|---|
| decanoyl peroxide | 60′ 20″ | 137′ | 1′ 36″ |
| benzoyl peroxide | 539′ | 343′ | 121′ |

* Molar ratio quinoline:peroxide 12·8

The increase of the decomposition rate of benzoyl peroxide going from unprotonated to a protonated quinoline is of the same order of magnitude as the increase of selectivity in competitive phenylations of protonated and unprotonated quinoline with nitrobenzene.[8] This would also indicate that the increase of decomposition rate of benzoyl peroxide must be due to a higher affinity of the phenyl radical towards the protonated base with some induced decomposition.

In conclusion the high decomposition rate of decanoyl peroxide in the presence of quinoline and other protonated heteroaromatic bases must be mainly ascribed to the nucleophilic character of the alkyl radical, which allows the complete capture of the nonyl radical escaping from the solvent "cage" and the consequent large induced decomposition. These results completely agree with those obtained from a study of the substituent effect on the alkylation rates,[1] which was interpreted in terms of transition state, similar to a $\pi$-complex in the reaction of the alkyl radicals with the protonated base.

The much smaller increase of decomposition rate with benzoyl peroxide in the presence of protonated quinoline also agrees with the low selectivity of the phenyl radical in respect to the polar influence of the substrata and the substituents: it can be better interpreted on the ground of a transition state similar to a $\sigma$-complex.

## EXPERIMENTAL

Most of the reagents were commercial products. Quinoline, acetic acid, heptane and benzene were distilled before the use and the purity was checked by GLC. Commercial decanoyl and benzoyl peroxides were crystallized twice. Valeroyl and isovaleroyl peroxides were prepared as previously described.[9] Combined gas-chromatography and mass spectrometry (GLC–MS) analyses were by a Perkin–Elmer Model 270 instrument at electron energy of 80 eV; source temperature 290°; accelerating voltage 2 KV: trap current 70 μA. Column conditions: 6 ft × $\frac{1}{8}$ inch steel column; 1·5% SE 30 on 80–100 mesh Chromosorb-W: 30 ml/min (helium): column temperature 80° (6 min) → 270, $\Delta t = 4°/\text{min}$.

*Decanoyl peroxide in heptane.* Decanoyl peroxide at a concentration of 0·2 mol was allowed to decompose in heptane under $N_2$ in a thermostat-bath at 70°. The mixture was extracted with 10% NaOH aq; the alkaline extract acidified and decanoic acid isolated. The heptane solution was directly analyzed by GLC–MS (Fig 1 and Table 1).

*Nonane and nonene*-1 were identified by comparison of MS of authentic samples: the separation by GLC was not complete: MS however indicates a large prevalence of nonane.

*The compounds* 2,3,4,5,6 *and* 7 in Fig 1 were identified as branched $C_{14}$ alkanes by MS. All the compounds show the molecular ion at *m/e* 198 and peaks of the fragments $C_nH_{2n+1}^{+}$, whose abundance is relatively higher when the fragments are formed by breaking a bond near a tertiary carbon atom. Abundant ions with odd electrons $C_nH_{2n}^{+\cdot}$ were also observed: these are characteristic of the fragmentation of branched alkanes, which have linear branches with more than 6 carbon atoms.[10]

*The compounds* 8,9 *and* 10 in Fig 1 were identified as branched $C_{16}$ alkanes by MS. All the compounds show the molecular ion peak at *m/e* 226 and a fragmentation pattern similar to that of $C_{14}$ alkanes.

*The compound* 12 of Fig 1 was identified as octadecane by comparison of MS of authentic sample. MS of the compound 11 shows the same molecular ion, 254, but a fragmentation pattern indicating the branched nature of the alkane.

*The compound* 13 in Fig 1 was identified as nonyl decanoate. MS shows the molecular ion peak at *m/e* 298 and significant peaks at *m/e* 173 (double hydrogen rearrangement[11]), 155 (decanoyl ion), 126 ($C_9H_{18}^{+\cdot}$), 61 (protonated acetic acid) and 60 ($CH_3COOH^{+}$ from two consecutive McLafferty rearrangements)

*Decanoyl peroxide in benzene.* The reaction was carried out as in heptane. GLC–MS shows in addition to nonane, nonene-1, octadecane and nonyl decanoate, two nonylbenzen isomers. The more abundant isomer was identified as 1-phenylnonane; its MS (Fig 5a) shows an intense molecular ion peak at *m/e* 204 and meets all the requirements of an unbranched 1-phenylalkane according to Grubb and Meyerson's scheme.[12] The other isomer was identified as 5-phenylnonane; its mass spectrum (Fig 5b) shows the molecular ion peak at *m/e* 204 and meets all the requirements of a branched α–C-alkylbenzene.[12] The very intense peak at *m/e* 147 (20% of the base peak at *m/e* 91 and the second peak in intensity of the spectrum) corresponds to the fragment originated by loss of $C_4H_9\cdot$ from the molecular ion through a benzylic cleavage. Small amounts of *o*, *m* and *p*-dinonylbenzenes (molecular ion peaks at *m/e* 330) were also formed. The results are summarized in Table 2.

*Decanoyl peroxide in acetic acid.* The reaction and the analysis were carried out as in heptane. Per cent ratios of nonane, nonene-1, octadecane and nonyl decanoate are shown in Table 3.

*Decanoyl peroxide in quinoline.* The reaction and the analysis were carried out as in heptane. The results are shown in Table 5. GLC–MS show the presence of at least five nonylquinoline isomers; only the 2-nonylquinoline is well separated: its MS shows the molecular ion peak at *m/e* 255 and significant peaks at 254 $(M-H)^+$, 156 (γ-cleavage) and 143 (β-cleavage with McLafferty rearrangement) according to the pattern observed with 2-n-butylquinoline.[13] Other four not well separated gaschromatographic peaks show the molecular ion at $m/e$ 255; no indication about the structure of these nonylquinoline isomers was obtained.

*Decanoyl peroxide in acetic acid and quinoline.* The reaction and the analysis were carried out as in heptane. With excess of quinoline, 2- and 4-nonylquinolines, decanoic acid and traces of octadecane were formed. 2,4-Dinonylquinoline was formed in considerable amount with ratios peroxide: quinoline > 1: its MS shows the molecular ion peak at $m/e$ 381. The ratios of octadecane and nonylquinolines with the change of quinoline concentrations are shown in Table 4. The structures of 2- and 4-quinolines and 2,4-dinonylquinoline were assumed on the ground of the results obtained with valeroyl peroxide under the same experimental conditions: only the known[2] 2- and 4-butylquinolines and 2,4-dibutylquinoline were formed. The structure of the 2-nonylquinoline was also confirmed by MS.

A run was carried out using commercial decanoyl peroxide with traces of 2,4,6-tri-t-butylphenol and an excess of quinoline (molar ratio quinoline: peroxide 12·8). By interrupting the reaction after 5 min. (Fig 4), GLC indicates that nonylquinolines are less than 50% of the products, the other products being nonane, nonene-1, octadecane and nonyl decanoate.

*Decomposition of isovaleroyl peroxide by copper salts in the presence of quinoline.* A solution of 7·8 g (0·0385 mol) of isovaleroyl peroxide in 30 ml of AcOH and 20 ml MeCN was dropped with $N_2$ flushing in a well stirred and refrigerated (0°) mixture of 7·7 g of cupric acetate (0·0385 mol), 5·5 g of cuprous oxide (0·0385), 5 g of quinoline (0·0385 mol) in 90 ml of AcOH and 60 ml of MeCN. Stirring was continued for 1 hr at 0° and 1 hr at room temperature. The mixture was basified with 10% NaOH and exhaustively extracted with ether. The solvent was removed and the residue (6·4 g) was analyzed by GLC. Four products were present: quinoline (30·5%), 2-isobutylquinoline (17%), 4-isobutylquinoline (23·5%) and 2,4-diisobutylquinoline (29%). The compounds were identified by comparison with authentic samples.[2]

*Kinetics.* The solvents were freed from dissolved $O_2$ by boiling them in a stream of $N_2$. Reactions were conducted under $N_2$ in closed vessels immersed in a thermostat bath at 70°. Samples were withdrawn at intervals and their peroxide contents determined iodometrically. Each run was carried out in duplicate.

First-order rate constants were obtained from the slopes of graphs of the logarithm of the peroxide concentration against time. With decanoyl peroxide in the presence of protonated quinoline these graphs were good straight lines (Fig 3) at high concentration of quinoline; at low quinoline: peroxide ratios the graphs deviated from linearity, as shown in Fig 2, and the first order rate constants were obtained from the initial slopes. Runs were carried out at 3 different concentrations of peroxide (0·2, 0·1 and 0·05 mol $l^{-1}$) without change of rate constants. The results are given in Tables 5, 6 and 7.

By using commercial, uncrystallized decanoyl peroxide with traces of inhibitor (2,4,6-tri-t-butylphenol) an induction period was observed (Fig 4). With crystallized peroxide the induction period was very short. Preliminary essays by using pyridine or quinoxaline in places of quinoline show analogous behaviour. With a ratio of decanoyl peroxide: pyridine 1:12·8 in AcOH (0·2 mol $l^{-1}$ in peroxide) the half life of the peroxide is 3′ 11″ at 70°. The comparison is however not very significant in these conditions owing to the different degree of protonation of the heteroaromatic bases in AcOH.

*Competitive alkylation of quinoline and benzene.* (a) 0·05 mol of decanoyl peroxide was allowed to decompose in a thermostat-bath at 70° in 1 mole of benzene and 0·2 mole of quinoline. The mixture was extracted with 10% NaOH aq and the benzene solution directly analyzed by GLC. The ratio of nonylquinoline: nonylbenzene is about 12; this value is approximate because the reaction is not clean and no check was made for determining the relative detector response in GLC.

(b) The experiment was carried out as in (a) in the presence of 1 mol of AcOH. Only negligible traces (< 0·5%) of nonylbenzene were observed by GLC.

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