Aerobic oxidation of saturated hydrocarbons into alkyl hydroperoxides induced by visible light and catalysed by a 'quinone–copper acetate' system[1,2]

Georgiy B. Shul'pin,* Marina M. Bochkova and Galina V. Nizova
N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4, ul. Kosygina, Moscow 117977, Russia

Irradiation in air of an alkane solution in MeCN in the presence of catalytic amounts of quinone and copper(II) acetate (ratio 5:1) affords mainly alkyl hydroperoxide which by the action of triphenylphosphine may be easily converted into the corresponding alcohol and ketone (aldehyde) (in the case of cyclohexane oxidation the ratio cyclohexanol:cyclohexanone was 50:1 after 10 h). The main peculiarities (the rate dependencies on initial concentrations of a substrate and the catalyst as well as of some additives and the effective activation energy) of the reaction are described. The proposed mechanism includes the abstraction of the hydrogen atom from alkane, RH, by photo-excited quinone to produce radicals $R^\bullet$ and $HOC_6H_4O^\bullet$. The former then reacts rapidly with O_2 to give $RO_2^\bullet$, and the latter may be reoxidized by copper(II). A copper(I) derivative thus formed may be converted into copper(II) when oxidized either by $RO_2^\bullet$ or O_2.

One of the tempting tasks of contemporary chemistry is to develop new methods for the aerobic highly selective oxidation of organic substances and especially hydrocarbons under mild conditions.[3] It seems that photochemical oxygenation with molecular oxygen (autooxidation) is a very useful method for the chemical transformation because in this case, the process usually takes place at ambient temperature and atmospheric pressure of dioxygen (or often even air). Photoinduced sensitized reactions of organic compounds with O_2 are very important as they are not only convenient synthetic routes[4] to valuable products (peroxides, ketones, acids, *etc.*), but also due to the fact that various biological systems apply light to stimulate the processes occurring in the living cell. For example, the oxidative interaction of DNA with ruthenium polypyridyl complexes[5a] or iron(III)[5b] promotes nucleic acid cleavage, and lipids may be photochemically peroxidized.[6] 'Photodynamic therapy'[7] based on the sensitized oxidation of biological matter in the target tissue is effective for the treatment of tumors,[8] *e.g.* cancer.[9] In general, sensitized light-stimulated processes often include an electron-transfer stage[10] and in many cases afford peroxides,[11] which are very valuable derivatives both for organic laboratories and industry,[12] and are well known to decompose easily upon heating[13] and may be relatively stable under the mild conditions employed in photochemical reactions.

Upon irradiation with high-energy UV light ($\lambda > ca.$ 200 nm), saturated hydrocarbons in the liquid phase (neat liquid alkane or a solution in 'inert' solvent, *e.g.* MeCN or $MeCO_2H$) are oxidized with atmospheric molecular oxygen,[14] but the rate of the reaction and yields of products are very low, especially if the hydrocarbon does not contain tertiary hydrogen atoms or aromatic ring activating benzylic C–H bonds. Alkylbenzenes are more reactive,[15] however in this case, the efficiency of the reaction is not high: the actual yield of the products of toluene oxidation after 24 h was only 0.15%.[15a]

In the presence of sensitizers the photo-oxidation rate is enhanced and longer wavelength light ($\lambda > ca.$ 300 nm) may be used. For the oxidation of C–H compounds, organic sensitizers can be divided into two types. Sensitizer, S, of the first type, upon irradiation is transformed into the singlet excited state which withdraws an electron from a substrate, RH [reaction (1)]. Here R is a group containing an aromatic ring.

$$S^* + RH \longrightarrow (S^{\bullet -}\ RH^{\bullet +}) \qquad (1)$$

Widely used sensitizers of this type are 9,10-dicyanoanthracene,[16] 1,4-dicyanonaphthalene,[17] various nitroaromatics and some other compounds.[18]

Photoexcited organic sensitizers of the second type [usually ketones in their lowest triplet state, $^3(n\pi^*)$][19] abstract a hydrogen atom from an alkane or alkyl group [reaction (2)].

$$S^* + RH \longrightarrow SH + R^\bullet \qquad (2)$$

Anthraquinone is a well known sensitizing reagent of this type;[2,20] acetone has also been used.[15a]

Earlier, we found that some inorganic complexes can catalyse efficiently the aerobic photo-oxidation of alkanes and arylalkanes in solution in MeCN or $MeCO_2H$. The compounds $FeCl_3$,[21] $CuCl_2$,[22] $HAuCl_4$,[23] polychromates,[24] iso- and heteropolyoxometalates[2,25] and UO_2Cl_2,[26] were used as photocatalysts. Ketones (aldehydes) and alcohols were formed as the main products in these reactions. In some cases the formation of alkyl hydroperoxides was also detected by GLC of the reaction samples before and after reduction with triphenylphosphine (*vide infra*), and the amounts of peroxides were comparable with those of final stable products, *i.e.* ketones (aldehydes) and alcohols. However, in no reaction catalysed by the metal compounds mentioned above, were peroxides the main constituents of the reaction mixture.

We report here on the quinone–copper acetate system which catalyses the mild photo-oxidation of alkanes, alkyl hydroperoxides being the predominant products of the reaction. A preliminary communication of this work has been published.[27] As previously briefly reported[28] aliphatic alcohols are also photo-oxidized by dioxygen in the presence of the same system to produce ketones or aldehydes.

Results and discussion

Anthraquinone is known to sensitize aerobic photo-oxidation of branched and cyclic alkanes and this reaction was even used to simulate degradation of petroleum components in sea water containing traces of anthraquinone under solar light.[20] This photo-oxidation leads to the formation of hydroxylated

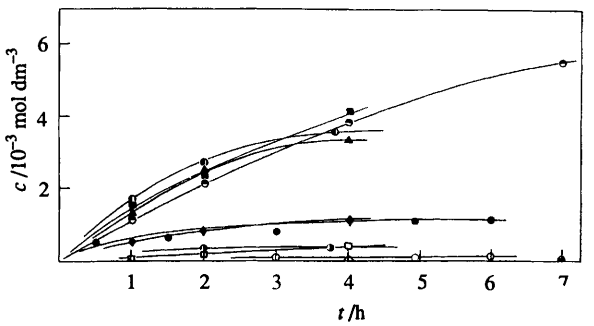


Fig. 1 Kinetics of the cyclohexane (0.46 mol dm^{-3}) oxidation by air in MeCN in the presence of quinone (10^{-3} mol dm^{-3}) (●, c-$C_6H_{11}OH$; ○, c-$C_6H_{10}O$) and $CuCl_2$ (■, c-$C_6H_{11}OH$; □, c-$C_6H_{10}O$), $Cu(ClO_4)_2$ (▲, c-$C_6H_{11}OH$; △, c-$C_6H_{10}O$), $Cu(MeCN)_4BF_4$ (◆, c-$C_6H_{11}OH$; ◇, c-$C_6H_{10}O$), $CuBr_2$ (◐, c-$C_6H_{11}OH$; ◑, c-$C_6H_{10}O$) and $FeCl_3$ (◓, c-$C_6H_{11}OH$; ◒, c-$C_6H_{10}O$). Concentration of each salt 0.2 × 10^{-3} mol dm^{-3}. Irradiation with two 150 W photo-lamps. Triphenylphosphine was added to an aliquot of the reaction solution before the GLC analysis (also in the cases shown in Figs. 2–7).

products, ketones and the products of cycle opening and isomerization. The authors proposed the formation of alkyl peroxides in this reaction, however these substances were not detected.

We have found that, unlike anthraquinone, quinone is a very poor sensitizing reagent. The kinetics of the photo-oxidation of cyclohexane in MeCN are shown in Fig. 1 (●, ○). As in our previous investigations, the process was monitored by withdrawing aliquots at specific intervals and analysing them by means of GLC. If the reaction solution was injected into the chromatograph without any preliminary treatment, the formation of cyclohexanol and cyclohexanone in approximately equal amounts was detected. The approximate equality of alcohol and ketone yields can by no means be interpreted as evidence for the presence of hydroperoxide in a reaction solution. In general, peroxide may be decomposed in the course of a reaction to produce approximately equal amounts of alcohol and ketone; this equality could, in certain cases, arise by coincidence in competitive reactions. However, in our case, if excess triphenylphosphine was added to the reaction solution 10–20 min before the GLC analysis, the resulting chromatogram differed drastically from that of a sample not subjected to reduction by triphenylphosphine. After the reduction, the cyclohexanol peak rose markedly, while the intensity of the cyclohexanone peak decreased. The sum of alcohol and ketone concentrations in the reduced sample was approximately equal to the total concentration of products in the solution untreated with triphenylphosphine. These results can be explained by the fact that in the reaction under discussion the alkane is oxidized to yield mainly cyclohexyl hydroperoxide. It is known that cyclohexyl hydroperoxide is totally decomposed in the chromatograph to produce cyclohexanol and cyclohexanone in the ratio *ca.* 1:1. The peroxide is readily and quantitatively reduced by triphenylphosphine to yield cyclohexanol.[29] Thus, by comparing the data of chromatographic analysis of the reaction solution before and after reduction by triphenylphosphine, the amounts of cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone present in the solution at a given moment can be estimated. For example, if the chromatogram of a solution before the reduction exhibits two peaks of approximately equal area for cyclohexanol and cyclohexanone and after the reduction only cyclohexanol is determined by GLC, these data testify that only cyclohexyl hydroperoxide is present in the solution.

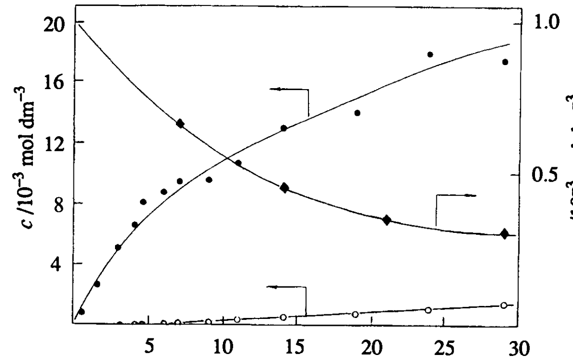


Fig. 2 Kinetics of the photochemical oxidation of cyclohexane (0.46 mol dm^{-3}) by air in MeCN in the presence of quinone (10^{-3} mol dm^{-3}) and $Cu(OAc)_2$ (0.2 × 10^{-3} mol dm^{-3}): ●, c-$C_6H_{11}OH$; ○, c-$C_6H_{10}O$; ◆, OC_6H_4O

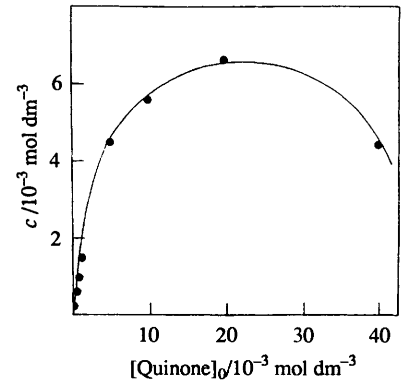


Fig. 3 Initial rate of the cyclohexane photochemical oxygenation (W_0; determined as concentration, c, of a sum of products after 1 h irradiation) *vs.* initial concentration of quinone; $[Cu(OAc)_2]$ = 0.2 × 10^{-3} mol dm^{-3}

Fig. 1 demonstrates that when the aerated cyclohexane solution in MeCN is irradiated in the presence of quinone, only a small amount (*ca.* 10^{-3} mol dm^{-3}) of cyclohexyl hydroperoxide is formed after 6 h. Here and in other experiments described in the present paper, light of incandescent tungsten lamps (λ > *ca.* 400 nm) was used for irradiation of the solutions placed into Pyrex vessels.

When quinone is combined with a salt (complex) of transition metal (the ratio quinone:salt is 5:1) the rate of cyclohexane photo-oxidation is enhanced (Fig. 1, ■, □, ▲, △, ◆, ◇, ◐, ◑, ◓, ◒). It seems that some amount of cyclohexyl hydroperoxide is decomposed in the course of the photo-reaction and small concentrations of cyclohexanone can be detected in the reaction aliquots after reduction with triphenylphosphine.

The best co-catalyst for photo-oxidation turned out to be copper acetate (Fig. 2). Indeed, in this case, the reaction proceeds with maximum rate and the selectivity is high (if the reaction solution is reduced with triphenylphosphine the ratio cyclohexanol:cyclohexanone is 50 after 10 h and 13 after 30 h). The accumulation of cyclohexanone started only after a long (*ca.* 10 h) period. Quinone, used as a sensitizer, was decomposed slowly and after 30 h its concentration was only one third of the initial concentration.

The dependencies of initial rates of the photo-reaction on concentrations of quinone (Fig. 3) and copper acetate (Fig. 4) exhibit maxima. At low cyclohexane concentration the reaction rate is proportional to the substrate concentration and when $[CyH]_0$ > 0.5 mol dm^{-3} this rate is almost independent of hydrocarbon concentration (Fig. 5). The initial rate of the reaction does not depend on temperature in the range 2–50 °C (the effective activation energy is less than 16 kJ mol^{-1}). The oxidation reaction reveals a primary kinetic hydrogen isotope effect, the value k_H/k_D being *ca.* 1.2 for [$^2H_6$]cyclohexane

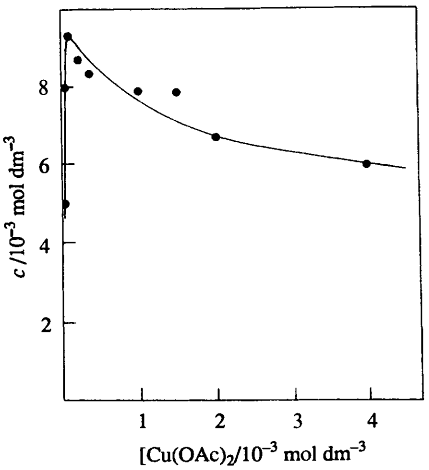


Fig. 4 Initial rate W_0 (see caption to Fig. 3) *vs.* [$Cu(OAc)_2$]; [quinone] = 10^{-3} mol dm^{-3}

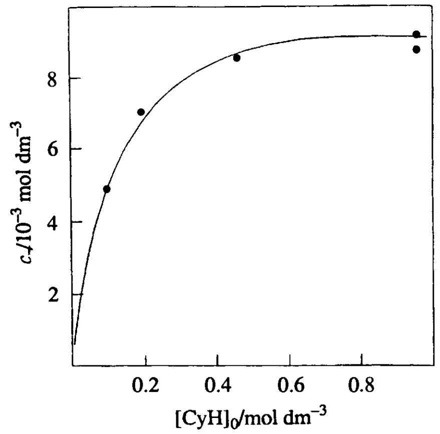


Fig. 5 Initial rate W_0 (see caption to Fig. 3) *vs.* [cyclohexane]; [$Cu(OAc)_2$] = 0.2×10^{-3} mol dm^{-3}; [quinone] = 10^{-3} mol dm^{-3}

(approximately the same values were obtained for photo-oxidation sensitized by anthraquinone and anthraquinone–copper acetate). Cyclohexane can also be oxidized by the system under discussion when acetonitrile is replaced with acetone as a solvent, the rate of oxidation being approximately the same.

Photo-oxidation of hexane (0.46 mol dm^{-3}) under the conditions described above gives a mixture of isomeric hexyl hydroperoxides identified after reduction with triphenylphosphine in the form of corresponding alcohols. Relative reactivities of the C–H bonds in hexane in positions 1, 2 and 3 (normalized taking into account the number of the hydrogen atoms at these positions) are 1 : 13 : 14 (for the photo-oxidation sensitized by anthraquinone the corresponding parameters are 1 : 70 : 50, *i.e.* the reaction is more selective). Photo-oxidation of 2-methylhexane also yielded a mixture of isomeric alcohols as detectable products. In this case normalized relative reactivities of the C–H bonds at primary, secondary and tertiary carbon atoms are 1° : 2° : 3° = 1 : 12 : 15 (for oxidation sensitized by anthraquinone 1° : 2° : 3° = 1 : 5 : 14).

Benzene is inert under the action of atmospheric oxygen during photo-irradiation in the presence of the system under discussion. In contrast, alcohols can be easily transformed into the corresponding aldehydes or ketones. Thus, propan-2-ol gives acetone; and cyclohexanol is oxidized to produce cyclohexanone (Fig. 6).

The following simplified mechanism may be proposed for the photo-reaction (Scheme 1). The first stage is the excitation of quinone by light (see refs. 14, 19, 20). The excited species is then capable of abstracting a hydrogen atom from alkane (or alcohol), RH, to produce alkyl radical R˙ and neutral semiquinone $HOC_6H_4O^{\cdot}$. The first radical is well known[30] to add molecular oxygen affording a new radical, $RO_2^{\cdot}$. This is a fast stage: the rate constants for reaction (3) at ambient

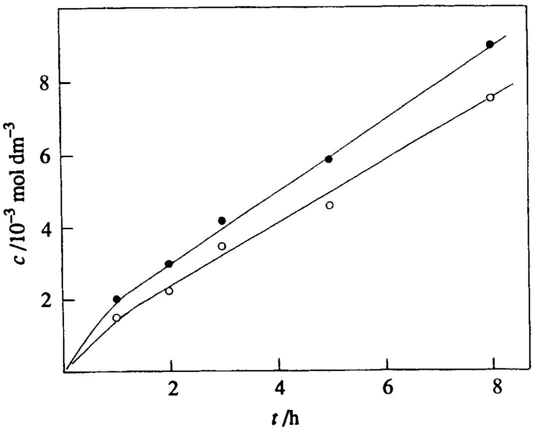
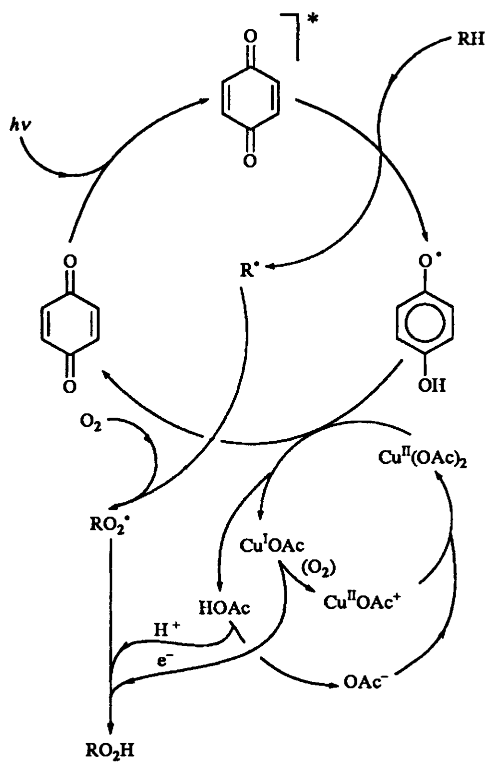


Fig. 6 Kinetics of accumulation of acetone (●) and cyclohexanone (○) in the photochemical oxidation of propan-2-ol (0.46 mol dm^{-3}) and cyclohexanol (0.46 mol dm^{-3}), respectively, by air in MeCN in the presence of quinone (10^{-3} mol dm^{-3}) and $Cu(OAc)_2$ (0.2×10^{-3} mol dm^{-3})



Scheme 1

$$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot} \quad (3)$$

temperature range from 10^6 up to 5×10^9 dm^3 mol s^{-1}; for the cyclohexyl radical this value is 3.4×10^9 dm^3 mol s^{-1} [see ref. 30(*a*)]. Phenoxyl radical, $HOC_6H_4O^{\cdot}$, may be reoxidized into quinone either by peroxyl radical, $RO_2^{\cdot}$ (this possible stage is not shown in Scheme 1) or by copper(II).[31a] Semiquinones QH˙ are known to react with radicals.[31a] Thus, the reaction (4)

$$QH^{\cdot} + Me_2C(OH)^{\cdot} \longrightarrow Q + Me_2CHOH \quad (4)$$

occurs in the cage during quinone photoreduction with an alcohol.[31b] Semiquinone radicals can also decay through bimolecular self-reactions (disproportionation) (5).[31c] The rate

$$\mathrm{QH}^{\bullet} + \mathrm{QH}^{\bullet} \longrightarrow \mathrm{Q} + \mathrm{QH_2} \qquad (5)$$

constant of this reaction (room temperature, in toluene) is 1.8×10^8 dm^3 mol^{-1} s^{-1} and the activation energy is only 16 kJ mol^{-1}.[31d] In the absence of active agents the dismutation reaction (6) of semiquinone radical anions is also possible.[31c]

$$\mathrm{Q}^{\bullet -} + \mathrm{Q}^{\bullet -} + 2\mathrm{H}^+ \longrightarrow \mathrm{Q} + \mathrm{QH_2} \qquad (6)$$

The route in which QH$^{\bullet}$ is oxidized with copper acetate seems to be predominant because in the absence of $\mathrm{Cu(OAc)_2}$ the yield of a product, $\mathrm{RO_2H}$, is very low (see Fig. 1, curve ●, ○). This is also a reason why we can ignore oxidation of $\mathrm{HOC_6H_4O^{\bullet}}$ into quinone by atmospheric oxygen.

In a special experiment, we have shown that hydroquinone [which might be produced in reactions (5) or (6)] can be easily oxidized by atmospheric oxygen in the dark in a MeCN solution if a catalytic amount of copper(II) acetate is present in the solution. The catalysis of hydroquinone oxidation by other copper complexes was described recently.[32] The copper(I) compound formed from copper(II) acetate may be reoxidized with atmospheric oxygen (see Scheme 1) or by $\mathrm{RO_2}^{\bullet}$ to produce $\mathrm{RO_2}^-$ which after addition of a proton is transformed into the product, $\mathrm{RO_2H}$. So, these stages explain the role of copper acetate in the photo-reaction: copper(II) reoxidizes a reduced form of organic sensitizer; a copper(I) derivative formed may be reoxidized in turn not only with $\mathrm{RO_2}^{\bullet}$ but also by $\mathrm{O_2}$. Indeed, copper(II) salts have been successfully employed as co-catalysts in oxidations by dioxygen and their role was to reoxidize a catalyst (transition metal ion).[3a,b,33]

In contrast to alkane photo-oxidation catalysed by other systems described by us earlier (*e.g.* $\mathrm{FeCl_3}$, $\mathrm{CuCl_2}$, *etc.*; see refs. 21–26), the reaction considered here gives rise to almost pure alkyl hydroperoxide. Such a feature may be explained by the fact that neither quinone nor copper acetate (or their combination) promote the rapid decomposition of alkyl hydroperoxide formed in the course of the reaction (some metal compounds[34] and even ketones in the presence of acids in acetonitrile[35] or quaternary ammonium salts[36] have been reported to accelerate decomposition of hydroperoxides). Indeed, Fig. 7 (top, curves ○, ●) shows that cyclohexyl hydroperoxide in the presence of quinone and copper acetate is decomposed rather slowly (half-life *ca.* 8 h). On the contrary, the half-life of the same peroxide in the presence of iron(III) chloride is only 0.5 h (Fig. 7, top, curves □, ■). It is evident that a special investigation is necessary to clarify the reason why peroxides are relatively inert toward copper acetate even under light irradiation.

It should be noted that the decomposition of alkyl hydroperoxide might initiate a radical chain autooxidation of a hydrocarbon. In order to investigate whether such a process really takes place we carried out photo-oxidation of cyclohexane under the action of the system considered in this paper in the absence and in the presence of cyclohexyl hydroperoxide. Fig. 7 (bottom, curves ●, ○ and ■, □) shows that when peroxide is added the rate of cyclohexane oxidation is not higher than in the absence of $\mathrm{CyO_2H}$. So, it may be concluded that the increment of the chain channel into the rate of oxidation is negligible.

In conclusion, irradiation of alkane solutions in MeCN in the presence of quinone and copper acetate causes smooth oxidation of the hydrocarbon by atmospheric oxygen to yield alkyl hydroperoxide which is stable under the conditions employed and is only very slowly decomposed to produce ketone (aldehyde) and alcohol. Alkyl hydroperoxide may be easily reduced by triphenylphosphine to alcohol and thus the described reaction provides a convenient method for the selective preparation of alcohols starting from saturated hydrocarbons.

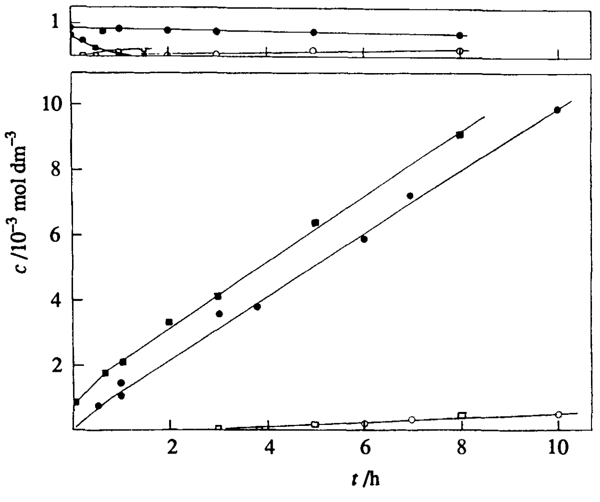


Fig. 7 Accumulation of cyclohexanol (filled symbols) and cyclohexanone (open symbols) in the photochemical reactions in MeCN in the presence of quinone (10^{-3} mol dm^{-3}) and $\mathrm{Cu(OAc)_2}$ (0.2×10^{-3} mol dm^{-3}): bottom, circle, oxidation of cyclohexane (0.46 mol dm^{-3}); square, the same in the presence of $\mathrm{CyO_2H}$ (0.9×10^{-3} mol dm^{-3}); top, circle, decomposition of $\mathrm{CyO_2H}$ dissolved in MeCN in the presence of quinone (10^{-3} mol dm^{-3}) and $\mathrm{Cu(OAc)_2}$ (0.2×10^{-3} mol dm^{-3}); square, the same as circle, but in the presence of $\mathrm{FeCl_3}$ (0.5×10^{-3} mol dm^{-3}) (irradiation with light of a street luminescent 125 W lamp, as for the oxidation reactions described in ref. 21)

Experimental

The photo-reactions were carried out in air in a glass vessel (volume of reaction solution 5 cm^3) surrounded by a water-cooling jacket (*ca.* 20 °C) with stirring, and using the full spectrum of two 150 W incandescent tungsten lamps ($\lambda >$ *ca.* 400 nm).

The process was monitored by withdrawing aliquots at specific intervals and analysing them by means of GLC (each sample was analysed twice, *i.e.* before and after the addition of triphenylphosphine). For the analysis, a LKhM-80/6 chromatograph ($l = 2$ m, 5% Carbowax 1500 on Inerton AW-HMDS, carrier gas Ar) was employed.

Acknowledgements

This work was financially supported by the International Science Foundation (grant no. MMS000), INTAS (grant no. 93-1226) and the Russian Basic Research Foundation (grant no. 93-03-5226). The authors thank Dr V. V. Lipes for the gift of a sample of pure cyclohexyl hydroperoxide.

References

1 Part 30 of the series ‘Photoinduced Reactions of Organic Compounds with Metal Complexes’.
2 Part 29, G. V. Nizova and G. B. Shul’pin, *Neftekhim.*, 1994, **34**, 364.
3 (*a*) R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981; (*b*) G. B. Shul’pin, *Organic Reactions Catalysed by Metal Complexes*, Nauka, Moscow, 1988; (*c*) *Activation and Functionalization of Alkanes*, ed. C. L. Hill, Wiley-Interscience, New York, 1933; (*d*) A. E. Shilov and G. B. Shul’pin, *Russ. Chem. Rev.*, 1987, **56**, 442; (*e*) A. E. Shilov and G. B. Shul’pin, *Russ. Chem. Rev.*, 1990, **59**, 853; (*f*) *Catalytic Selective Oxidation*, eds. S. T. Oyama and J. W. Hightower, ACS, New York, 1993; (*g*) *New Developments in Selective Oxidation*, eds.

G. Centi and F. Trifiro, Elsevier, Amsterdam, 1990; (*h*) R. S. Drago, *Coord. Chem. Rev.*, 1992, **117**, 185; (*i*) D. Mansuy, *Coord. Chem. Rev.*, 1993, **125**, 129; (*j*) *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*, eds. D. H. R. Barton, A. E. Martell and D. T. Sawyer, Plenum Press, New York, 1993.

4 J. Mattay, *Synthesis*, 1989, 133; J. Julliard and M. Channon, *Bull. Soc. Chim. Fr.*, 1992, **129**, 242; M. Chanon, M. Julliard, J. Santamaria and F. Chanon, *New J. Chem.*, 1992, **16**, 171; T. Toshiyuki, K. Mizumo, I. Hashida and Y. Otsuji, *Chem. Lett.*, 1992, 781.

5 (*a*) J.-P. Lecomte, A. Kirsch-De Mesmaeker, J. M. Kelly, A. B. Tossi and H. Görner, *Photochem. Photobiol.*, 1992, **55**, 681; (*b*) R. A. Larson, R. E. Lloyd, K. A. Marley and R. W. Tuveson, *J. Photochem. Photobiol., B: Biol.*, 1992, **14**, 345.

6 A. W. Girotti, *Photochem. Photobiol.*, 1990, **51**, 497; D. Z. Marcovic, T. Durand and L. K. Patterson, *Photochem. Photobiol.*, 1990, **51**, 389; G. J. Bachowski, T. J. Pintar and A. W. Girotti, *Photochem. Photobiol.*, 1991, **53**, 587.

7 *Photodynamic Therapy*, eds. B. W. Henderson and T. J. Dougherty, Dekker, New York, 1992; B. W. Henderson and T. J. Dougherty, *Photochem. Photobiol.*, 1992, **55**, 145; K. Tenchner, A. Pgarrher, H. Stiel, W. Freyer and D. Lenpold, *Photochem. Photobiol.*, 1993, **57**, 465.

8 G. Jori and E. Reddi, *Light Biol. Med.*, 1991, 253.

9 J. Moan and K. Berg, *Photochem. Photobiol.*, 1992, **55**, 931.

10 J. C. W. Chien, *J. Phys. Chem.*, 1965, **69**, 4317; M. Chanon, M. Rajzman and F. Chanon, *Tetrahedron*, 1990, **46**, 6193; T. Tamai, K. Mizuno, I. Hashida and Y. Otsui, *Photochem. Photobiol.*, 1991, **54**, 23; B. M. Monroe and G. C. Weed, *Chem. Rev.*, 1993, **93**, 435.

11 T. Tamai, K. Mizuno, I. Hashida and Y. Otsuji, *J. Org. Chem.*, 1992, **57**, 5338; T. Tamai, K. Mizuno, I. Hashida and Y. Otsuji, *Tetrahedron Lett.*, 1993, **34**, 2641; W. Adam, X. Qian and C. R. Saha-Möller, *Tetrahedron*, 1993, **49**, 417; J. V. Castell, M. J. Gomez-Lechon, C. Grassa, L. A. Martinez, M. A. Miranda and P. Tarrega, *Photochem. Photobiol.*, 1993, **57**, 486.

12 See, *e.g.* A. Goosen, C. W. McCleland, D. H. Morgan, J. S. O'Connell and A. Ramplin, *J. Chem. Soc., Perkin Trans. 1*, 1993, 401; P. H. Dussault and M. R. Hayden, *Tetrahedron Lett.*, 1992, **33**, 443; R. K. Haynes and S. C. Vonwiller, *J. Chem. Soc., Chem. Commun.*, 1990, 1102; J. L. Courtneidge, *J. Chem. Soc., Chem. Commun.*, 1992, 381; J. L. Courtneidge, *J. Chem. Soc., Chem. Commun.*, 1992, 1270; A. J. Bloodworth, C. J. Cooksey and D. Korkodilos, *J. Chem. Soc., Chem. Commun.*, 1992, 926; J. L. Courtneidge and M. Bush, *J. Chem. Soc., Perkin Trans. 1*, 1992, 1531; J. L. Courtneidge, M. Bush and L.-S. Loh, *J. Chem. Soc., Perkin Trans. 1*, 1992, 1539; D. E. Patton and R. S. Drago, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1611; P. H. Dussault and I. Q. Lee, *J. Am. Chem. Soc.*, 1993, **115**, 6458; C. W. Jefford, *Chem. Soc. Rev.*, 1993, 59.

13 *The Chemistry of Peroxides*, ed. S. Patai, Wiley, Chichester, 1983.

14 J. A. Barltrop and J. D. Coyle, *Excited States in Organic Chemistry*, Wiley, New York, 1975.

15 (*a*) M. Pasternak and A. Morduchowitz, *Tetrahedron Lett.*, 1983, **24**, 4275; (*b*) L. K. Sydnes, I. C. Burkow and S. H. Hansen, *Acta Chem. Scand., Ser. B*, 1985, **B 39**, 829.

16 I. Saito, K. Tamoto and T. Matsuura, *Tetrahedron Lett.*, 1979, **31**, 2889; K. Mizuno, K. Yoshioka and Y. Otsuji, *Chem. Lett.*, 1983, 941; K. Mizuno, N. Ichinose and Y. Otsuji, in *The Role of Oxygen in Chemistry and Biochemistry*, eds. W. Ando and Y. Moro-oka, Elsevier, Amsterdam, 1988, p. 79; S. Futamura and Y. Kamiya, in *The Role of Oxygen in Chemistry and Biochemistry*, eds. W. Ando and Y. Moro-oka, Elsevier, Amsterdam, 1988, p. 85; K. Gollnick, X.-L. Xiao and U. Paulmann, *J. Org. Chem.*, 1990, **55**, 5945; K. Gollnick and U. Paulmann, *J. Org. Chem.*, 1990, **55**, 5954; J. Santamaria, R. Jroundi and J. Rigaudy, *Tetrahedron Lett.*, 1989, **30**, 4677; M. A. Kellett and D. G. Whitten, *J. Am. Chem. Soc.*, 1991, **113**, 358; R. C. Kanner and C. S. Foote, *J. Am. Chem. Soc.*, 1992, **114**, 682; J. Santamaria and R. Jroundi, *Tetrahedron Lett.*, 1991, **34**, 4291.

17 A. Albini and S. Spreti, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1175.

18 M. Julliard, *New J. Chem.*, 1994, **18**, 243; R. Akaba, M. Kamata, H. Itoh, A. Nakao, S. Goto, K. Saito, A. Negishi, H. Sakuragi and K. Tokumaru, *Tetrahedron Lett.*, 1992, **46**, 7011.

19 B. Zhou and P. J. Wagner, *J. Am. Chem. Soc.*, 1989, **111**, 6796; D. Sengupta, R. Sumathi and A. K. Chandra, *New J. Chem.*, 1991, **15**, 901; Y. Tanimoto, M. Uehara, M. Takashima and M. Itoh, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 3121.

20 J.-F. Rontani and G. Giusti, *J. Photochem. Photobiol., A: Chem.*, 1987, **40**, 107; 1989, **46**, 347; 1990, **53**, 69.

21 G. B. Shul'pin and M. M. Kats, *React. Kinet. Catal. Lett.*, 1990, **41**, 239; G. B. Shul'pin, G. V. Nizova and M. M. Kats, *Zh. Obshch. Khim.*, 1990, **60**, 2730; G. B. Shul'pin and M. M. Kats, *Neftekhim.*, 1991, **31**, 648; G. B. Shul'pin and A. N. Druzhinina, *Mendeleev Commun.*, 1992, 36; G. B. Shul'pin and G. V. Nizova, *Neftekhim.*, 1993, **33**, 118.

22 G. B. Shul'pin, G. V. Nizova and M. M. Kats, *Neftekhim.*, 1991, **31**, 658; P. Lederer, G. V. Nizova, M. M. Kats and G. B. Shul'pin, *Coll. Czech. Chem. Commun.*, 1992, **57**, 107.

23 G. V. Nizova and G. B. Shul'pin, *Neftekhim.*, 1992, **32**, 37.

24 G. B. Shul'pin, A. N. Druzhinina and G. V. Nizova, *Izvest. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2463; G. V. Nizova, G. V. Losenkova and G. B. Shul'pin, *React. Kinet. Catal. Lett.*, 1991, **45**, 27; G. B. Shul'pin and A. N. Druzhinina, *Neftekhim.*, 1993, **33**, 256.

25 G. B. Shul'pin and M. M. Kats, *Bull. Acad. Sci. USSR, Div., Chem. Sci.*, 1989, **38**, 2205; G. B. Shul'pin and M. M. Kats, *Zh. Obshch. Khim.*, 1989, **59**, 2738.

26 G. V. Nizova and G. B. Shul'pin, *Zh. Obshch. Khim.*, 1990, **60**, 2124.

27 G. B. Shul'pin and A. N. Druzhinina, *React. Kinet. Catal. Lett.*, 1992, **47**, 207.

28 G. Süss-Fink and G. B. Shul'pin, *Izvest. Russ. Akad. Nauk, Ser. Khim.*, 1994, 1147.

29 L. G. Galimova, S. I. Maslennikov and A. I. Nikolaev, *Izvest. Akad. Nauk SSSR, Ser. Khim.*, 1980, 2464; G. B. Shul'pin and G. Süss-Fink, *J. Chem. Soc., Perkin Trans. 2*, 1995, **7**, 1459.

30 (*a*) B. Maillard, K. U. Ingold and J. C. Scaiano, *J. Am. Chem. Soc.*, 1983, **105**, 5095; (*b*) Q. J. Niu and G. D. Mendenhall, *J. Am. Chem. Soc.*, 1992, **114**, 165; (*c*) R. K. Jensen, S. Korcek and M. Zinbo, *J. Am. Chem. Soc.*, 1992, **114**, 7743; (*d*) G. E. Quelch, M. M. Gallo and H. F. Schaefer, III, *J. Am. Chem. Soc.*, 1992, **114**, 8239; (*e*) O. Dobis and S. W. Benson, *J. Am. Chem. Soc.*, 1993, **115**, 8798.

31 (*a*) E. A. Denisov and I. V. Khudyakov, *Chem. Rev.*, 1987, **87**, 1313; (*b*) L. A. Margulis, I. V. Khudyakov and V. A. Kuz'min, *Chem. Phys. Lett.*, 1985, **119**, 244; (*c*) I. V. Khudyakov and V. A. Kuz'min, *Usp. Khim.*, 1975, **44**, 1748; (*d*) A. J. Elliot, K. Legan and J. K. S. Wan, *J. Chem. Soc., Faraday Trans. 1*, 1978, 2111.

32 D. A. Rockcliffe and A. E. Martell, *Inorg. Chem.*, 1993, **32**, 3143.

33 See, *e.g.* Y. Fujiwara, T. Jintoku and K. Takaki, *CHEMTECH*, 1990, 636; A. Kunai, T. Wani, Y. Uehara, F. Iwasaki, Y. Kuroda, S. Ito and K. Sasaki, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2613.

34 C. A. Tolman, J. D. Druliner, P. J. Krusic, M. J. Nappa, W. C. Seidel, I. D. Williams and S. D. Ittel, *J. Mol. Catal.*, 1988, **48**, 129; H. Sawada, H. Ishigaki, M. Kato and M. Nakayama, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 785; C. B. Hansen, G. J. Hoogers and W. Drenth, *J. Mol. Catal.*, 1993, **79**, 153.

35 L. V. Petrov, T. I. Drozdova, L. Ya. Lyuta and V. M. Solyanikov, *Izvest. AN SSSR, Ser. Khim.*, 1990, 278.

36 E. Napadensky and Y. Sasson, *J. Chem. Soc., Chem. Commun.*, 1991, 65.

Paper 4/07450E
Received 6*th December* 1994
Accepted 9*th February* 1995