

UNUSUAL SELECTIVITY IN PHOTOOXYGENATION OF ALKANES BY AIR
IN CH₃CN SOLUTIONS CATALYZED BY CrCl₃-
-C₆H₅CH₂N(C₂H₅)₃Cl

G.V. Nizova, G.V. Losenkova and G.B. Shul'pin*
Institute of Chemical Physics, Moscow 117977, USSR

Received January 15, 1991
Accepted March 14, 1991

A new system Cr Cl₃-C₆H₅CH₂N(C₂H₅)₃Cl-CH₃CN for photo-oxygenation of alkanes is suggested. Unlike metal chlorides and oxocomplexes, it oxidizes alkanes to produce ketones and small amounts of alcohol. Adding of benzene, methylene chloride or ethanol to the cyclohexane solution rises the oxygenation rate and changes the ketone/alcohol ratio. With small amounts of hydroquinone the formation rate of cyclohexanone (but not of cyclohexanol) sharply decreases. Kinetic isotope effect in the oxidation of C₆H₁₂ and C₆D₁₂ is ~ 1 for cyclohexanol and ~ 2.9 for cyclohexanone. Cyclohexanol formation is assumed to follow a mechanism that does not involve free radicals. Free radicals can participate in the route toward ketone.

Описывается новая система CrCl₃-C₆H₅CH₂N(C₂H₅)₃Cl-CH₃CN для фотооксигенирования алканов. В отличие от хлоридов металлов и оксокомплексов, она окисляет алканы с образованием кетонов и небольших количеств спирта. Добавление в раствор циклогексана бензола, метиленхлорида или этанола ускоряет оксигенирование и изменяет соотношение кетон/спирт. В присутствии небольших количеств гидрохинона скорость образования циклогексанона (но не циклогексанола) резко понижается. Кинетический изотоп-

* Author for correspondence

ный эффект окисления C_6H_{12} и $C_6D_{12} \sim 1$ для циклогексанола и $\sim 2,9$ для циклогексанона. Предполагается, что образование циклогексанола протекает по механизму, который не включает участия свободных радикалов. Свободные радикалы могут участвовать в маршруте, приводящем к кетону.

Recently, we have suggested a series of systems to catalyze the oxygenation of alkanes and arylalkanes by air dioxygen under irradiation. These systems contain transition metal chlorides $FeCl_3$ [1-3], $CuCl_2$ [4], $AuCl_4^-$ [5] as well as $RhCl_3$, $RuCl_3$, $PtCl_6^{2-}$ [6] (refer also to the recent review on C-H bond activation [7]). Various organic solvents (CH_3COOH , CH_3CN , CH_3COCH_3) were used, and alkylammonium salts were added to CH_2Cl_2 solutions to solubilize metal halides. In all cases the oxygenation of cyclohexane, toluene and ethylbenzene yields the corresponding ketone and alcohol in approximately equal amounts. The same ketone/alcohol ratio was found in the photooxygenation reactions catalyzed by $Cr_2O_7^{2-}$, $Cr_4O_{13}^{2-}$ [6,8], VO_3^- , $PW_{12}O_{40}^{3-}$ [9] in CH_2Cl_2 (similar systems based on oxo-complexes as photocatalysts were described in Refs [10-11]).

We have found that alkanes and arylalkanes can be effectively oxygenated by air dioxygen if their solutions in CH_3CN are irradiated in the presence of catalytic amounts of $CrCl_3 \cdot 10H_2O$ and $C_6H_5CH_2N(C_2H_5)_3Cl$ (in the absence of alkylammonium salt, $CrCl_3$ insoluble in organic solvents). A source of irradiation was a luminescent street lamp. Reactions were carried out in air in a Pyrex cylindrical vessel with a water-cooled ($10^\circ C$) jacket under stirring. Products were identified by gas-liquid chromatography.

The main peculiarity of this system is the prevalence of ketone in the oxidation products of hydrocarbons. Kinetics of cyclohexane photooxidation is illustrated in Fig. 1. The induction period in the accumulation of oxidation products can be reduced if the solution is irradiated before adding the substrate.

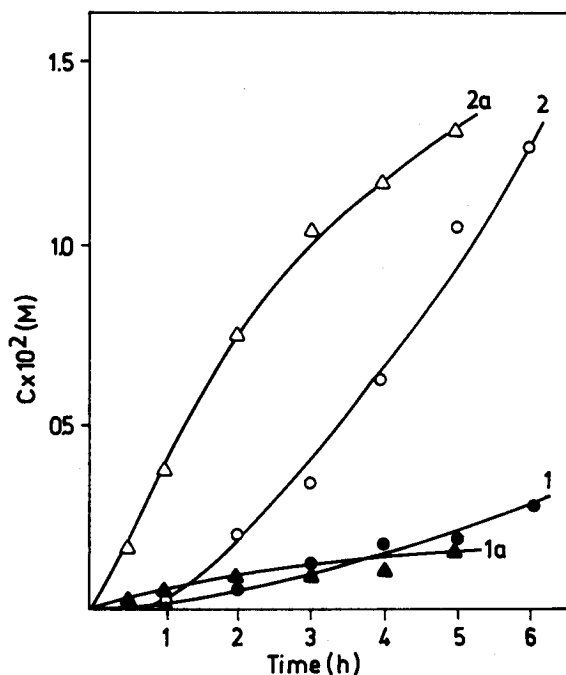


Fig. 1. Kinetics of cyclohexane (0.46 M) photooxygenation in CH_3CN solution in the presence of $\text{CrCl}_3 \cdot 10\text{H}_2\text{O}$ ($2.5 \times 10^{-4}\text{M}$) and $\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_3\text{Cl}$ ($7.5 \times 10^{-4}\text{M}$).

1 - Cyclohexanol, 2 - cyclohexanone: a - Irradiation for 2.5 h before adding cyclohexane

The yields of cyclohexanol and cyclohexanone increase linearly with increasing concentrations of cyclohexane (within 0-0.92 M) or catalyst (within 0- $1.0 \times 10^{-3}\text{M}$). Photooxygenation rate is proportional to light intensity. Kinetic isotope effects $k_{\text{H}}/k_{\text{D}}$ are equal to ~ 1 for cyclohexanol and ~ 2.9 for cyclohexanone.

In contrast to cyclohexane photooxygenation catalyzed by FeCl_3 and CuCl_2 , the oxidation rate in the presence of CrCl_3 and $\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_3\text{Cl}$ catalysts depends on temperature. At $T=3-26^\circ\text{C}$ the calculated effective activation energy for cyclohexanone formation equals ~ 20 kcal/mol.

The second principal peculiarity of the suggested system, greatly distinguishing it from those based on FeCl_3 and CuCl_2 , is the kinetic dependence on various additives. Kinetic curves for the accumulation of cyclohexanol and cyclohexanone in photooxygenation catalyzed by $\text{CrCl}_3\text{-C}_6\text{H}_5\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_3\text{Cl}$ are illustrated in Figs 2-4.

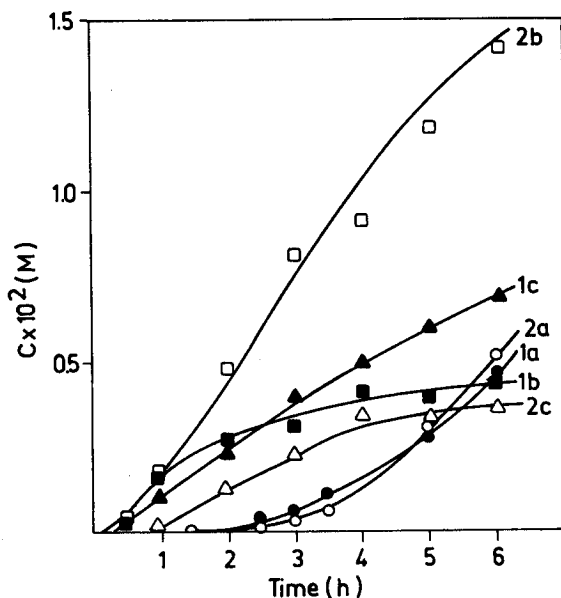


Fig. 2. Kinetics of cyclohexane photooxidation by CrCl_3 system (for concentrations, see Fig. 1)
 a - reaction in acetone, b - in $\text{CH}_3\text{CN-C}_6\text{H}_6$ (4:1 vol.),
 c - in $\text{CH}_3\text{CN-CH}_2\text{Cl}_2$ (1:8.5 vol.)

It can be seen that in acetone solution the oxidation takes place with a long induction period, and in this case, the ketone/alcohol ratio is ~ 1 . In the presence of large amounts of CH_2Cl_2 the predominant oxidation product is cyclohexanol. p-Quinone or hydroquinone also change greatly the ketone/alcohol ratio. The formation rate of cyclohexanone decreases, whereas that of

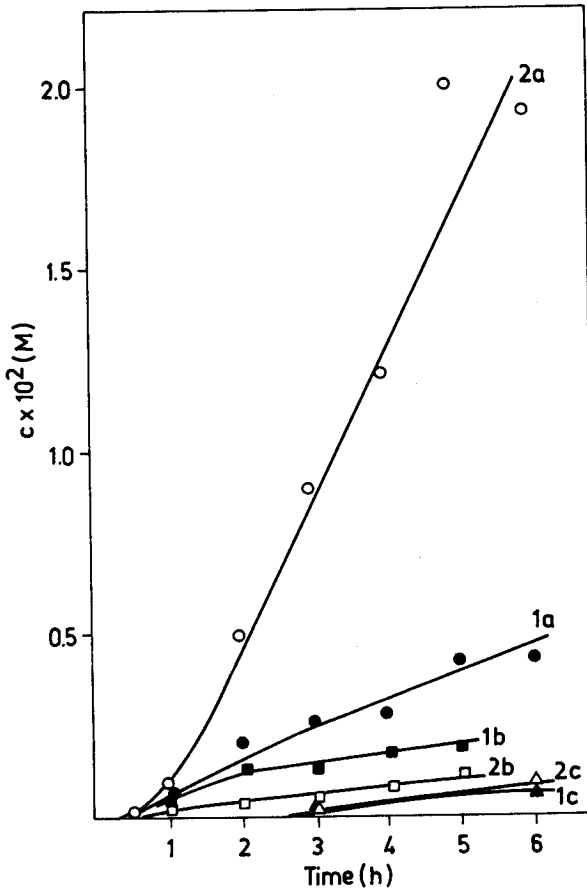


Fig. 3. Kinetics of cyclohexane photooxidation (for conditions see Fig. 1) in the presence of: a - C_2H_5OH (2.3×10^{-3} M), b - p-quinone (2.2×10^{-3} M), c - 2,2'-bipyridyl (2.0×10^{-3} M)

cyclohexanol remains almost unchanged. Moreover, in the presence of quinone the induction period in cyclohexanol accumulation decreases (Figs 3 and 1). The addition of 2,6-di-*t*-butyl-4-methylphenol also changes the ketone/alcohol ratio, but the effect of this additive is observed only during the first 3 hours of irradiation (compare Figs 4 and 1). In the presence

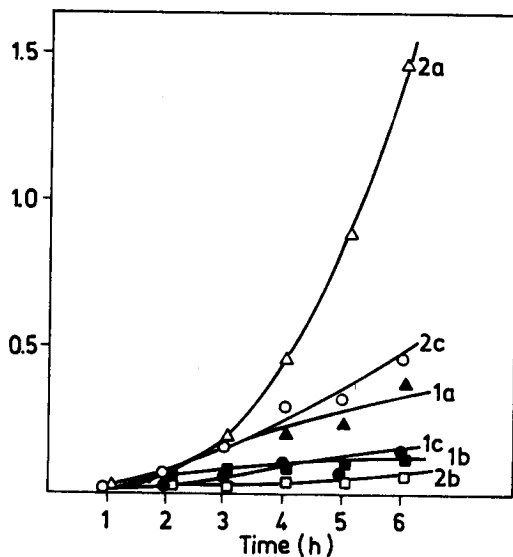


Fig. 4. Kinetics of cyclohexane photooxidation (conditions as in Fig. 1) in the presence of: a - 2,6-bis(t-butyl)-4-methylphenol (2.0×10^{-3} M), b - hydroquinone (2.2×10^{-3} M), c - methyl methacrylate (2.0×10^{-3} M)

of methyl methacrylate the accumulation rate of cyclohexanone diminishes, whereas that of cyclohexanol remains practically unchanged. Finally, 2,2'-bipyridyl inhibits the formation of both cyclohexanone and cyclohexanol. It is interesting that the addition of small amounts of ethanol (or cyclohexanol) increases the formation rate of both cyclohexanone and cyclohexanol. Neither CCl_4 nor $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{OOH}$ produce any significant effect on the rate of cyclohexane photooxygenation.

Note that in the cases of FeCl_3 and CuCl_2 systems (alkylammonium salt was also added) the ketone/alcohol ratio is 1 and the addition of hydroquinone, 2,6-di-t-butyl-4-methylphenol and methyl methacrylate does not affect (or slightly diminishes) the accumulation rate of cyclohexane oxidation products.

The rate of n-hexane oxygenation by the CrCl_3 system is much lower than that for cyclohexane. n-Hexane (0.46 M) in CH_3CN after 40 h irradiation and subsequent reduction of the reaction mixture by NaBH_4 yields hexan-1-ol (2.4×10^{-4} M), hexan-2-ol (4.2×10^{-4} M) and hexan-3-ol (5.3×10^{-4} M). Unreduced reaction mixture contains only negligible amounts of alcohols. 2-Methylbutane in CH_3CN after 17 h irradiation produces a mixture of aldehydes, ketone and tert-alcohol, the relative selectivities per C-H bond are $1^\circ : 2^\circ : 3^\circ \approx 1:14:9$.

After 6 h irradiation, toluene (0.46 M) is oxidized mainly to benzaldehyde. The reaction mixture contains 1.6×10^{-2} M benzaldehyde and only 0.2×10^{-2} M benzyl alcohol, even if the mixture $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$ (3.8:1 v/v) was used as a solvent. Benzaldehyde is also the main product (1.02×10^{-2} M after 6 hours irradiation) of styrene oxygenation under the same conditions, with the total yield of acetophenone and styrene oxide amounting to 0.15×10^{-2} M. Cyclohexanol (4.6×10^{-2} M) is oxidized to cyclohexanone (0.8×10^{-2} M) in a given catalytic system after 6 h irradiation.

In conclusion, it should be emphasized that the oxygenation mechanism of alkanes by $\text{CrCl}_3-\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_3\text{Cl}$ is likely to be significantly different compared to that in the systems containing FeCl_3 or CuCl_2 . One may assume that the mechanism in the two latter cases is essentially pseudoradical (or even molecular), whereas in the chromium systems alkane oxygenation to ketone involves the participation of free radicals. Alcohol formation apparently follows a different route without the participation of free radicals.

We have also found that $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of $\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_3\text{Cl}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in CH_3CN are inactive as catalysts for the photooxygenation of alkanes by air dioxygen.

REFERENCES

1. G.B. Shul'pin, M.M. Kats, P. Lederer: Zh. Obshch. Khim., 59, 2742 (1989).

2. G.B. Shul'pin, M.M. Kats: *React. Kinet. Catal. Lett.*, 41, 239 (1990).
3. G.B. Shul'pin, G.V. Nizova, M.M. Kats: *Zh. Obshch. Khim.*, 60, 2730 (1990).
4. G.V. Nizova, M.M. Kats, G.B. Shul'pin: *Izv. Akad. Nauk SSSR, ser. khim.*, 698 (1990).
5. G.B. Shul'pin, G.V. Nizova, A.N. Druzhinina, M.M. Kats: *Proc. 7th Intern. Symp. on Homogeneous Catalysis (Abstracts)*, Lyon, France, 1990.
6. A.E. Shilov, G.B. Shul'pin: *Usp. Khim.*, 59, 1468 (1990).
7. G.B. Shul'pin, G.V. Nizova, A.N. Druzhinina: *Oxid. Commun.* (in press).
8. G.B. Shul'pin, M.M. Kats: *Izv. Akad. Nauk SSSR, ser. khim.* 2390 (1989).
9. R.C. Chambers, C.L. Hill: *Inorg. Chem.*, 28, 2509 (1989).
10. D. Attanasio, L. Suber: *Inorg. Chem.*, 28, 3779 (1989).
11. N.Z. Muradov, M.I. Rustamov: *Kinet. Katal.*, 30, 248 (1989).