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Lewis acidic complexes of platinum(II): a mechanistic study of the Baeyer–Villiger oxidation of methylcyclohexanone with hydrogen peroxide catalyzed by [(triphosPO)Pt]$^{2+}$ species

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Abstract

A kinetic study of the Baeyer–Villiger epoxidation of methylcyclohexanone with 35% hydrogen peroxide catalyzed by [(triphos-PO)Pt(CH_2Cl_2)]$^{2+}$ is reported based on initial rate analysis. The mechanism suggested involves coordination of the ketone to the coordinatively unsaturated complex, followed by nucleophilic attack of free hydrogen peroxide. The importance of the Lewis acid character of the metal center is crucial in promoting the activation of the substrate as well as its ability to facilitate the leaving of the otherwise bad OH$^-$ leaving group from the intermediate *quasi*-peroxymetallacycle.

Keywords: Platinum; Lewis acids; Homogeneous catalysis; Oxidation; Peroxides

1. Introduction

The idea of using electron-rich metal centers like Pd(II) and Pt(II) as Lewis acid catalysts is a relatively recent one [1]. Indeed, the common view about these species is to consider them more as bases rather than acids. However, it has been observed that the Lewis acidity of these systems can be actually exploited, provided that at least one positive charge is present on the complex. In the past few years, the number of applications of these systems in homogeneous catalysis has been increasing [1]. Despite a long lasting involvement in homogeneous catalytic oxidation with Pt(II) complexes, it was only relatively recently [1a] that we realized the importance of Lewis acidity in the promotion of such reactions. This was clearly elucidated very recently [2] by comparing the behavior of complexes significantly differing in this property.

We have studied [2] a class of cationic complexes of Pt(II) of the type [(P–P–P)PtX]$^{n+}$ and [(P–P–O)PtX]$^{n+}$ (P–P–P = triphos; P–P–O = triphosPO; X = solvent, OH, OOH; $n = 1, 2$) and have found that they are considerably Lewis acidic. This property was found crucial for their selectivity properties as they preferentially promote the Baeyer–Villiger oxidation of ketones versus the epoxidation of olefins in substrates containing both functional groups (see in Scheme 1 the case of dihydrocarvone). In competitive experiments carried out either with olefins and ketones in the same batch or in the presence of unsaturated ketones, their selectivity towards the oxidation of the carbonyl group was found to be complete [2].

The Baeyer–Villiger oxidation of ketones is widespread in organic synthesis [3] but quite elusive catalytically [4] as the properties necessary for a catalyst to be active are unclear. Hence, having established a clear correlation with the Lewis acidity of the metal complex can be very important for the development of new, more effective and selective catalytic systems.

On this basis, we thought of interest to corroborate the above observations, based only on reactivity studies, with a mechanistic investigation that helps in clarifying the exact role of the metal. For this reason, we report here a kinetic analysis of the oxidation of methylcyclohexanone, taken as prototype substrate, with 35% hydrogen peroxide using [(P–P–O)Pt(acetone)](BF_4)$_2$ as catalyst, i.e. the complex that proved most active in the oxidation reaction.

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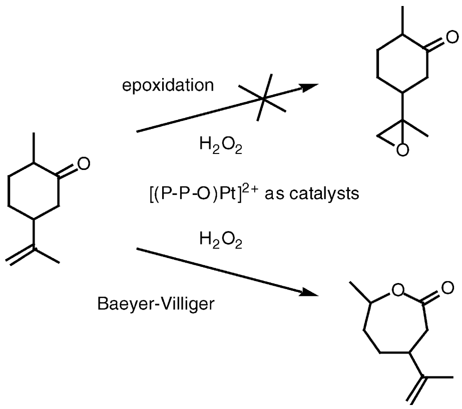
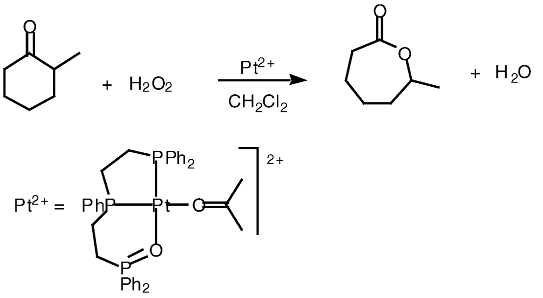


Scheme 1.



Scheme 2.

2. Results and discussion

The reaction studied is shown in Scheme 2 and it is two-phase (H_2O/CH_2Cl_2). This was chosen because a screening of the best reaction conditions, already performed previously [2], indicated that the reaction can be conveniently carried out at room temperature with easily detectable reaction rates. In the present work, all experiments were carried out at 20 °C, a temperature at which side reactions can be minimized. A typical reaction profile showing the formation of 2-heptalactone versus time is reported in Fig. 1. No other products are formed during the course of the reaction. As can be seen, the initial rate remains constant for about 1 h and can be determined with reasonable accuracy. The initial rate was analyzed as a function of the concentrations of the reaction different reactants. Due to the possible effect of H^+, all reactions were carried out at pH 1.5 by buffering with $KHSO_4/K_2SO_4$.

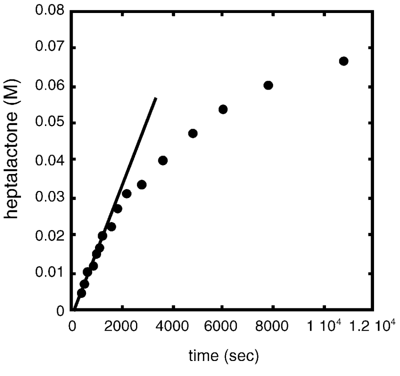


Fig. 1. A typical lactone concentration vs. time progress in the Baeyer–Villiger oxidation of methylcyclohexanone with 35% hydrogen peroxide catalyzed by $[(triphosPO)Pt(CH_2Cl_2)]^{2+}$. Experimental conditions: $[Pt]_T$ 4.42×10^{-3} M, [methylcyclohexanone] 0.367 M, $[H_2O_2]_{org}$ 15.5×10^{-2} M.

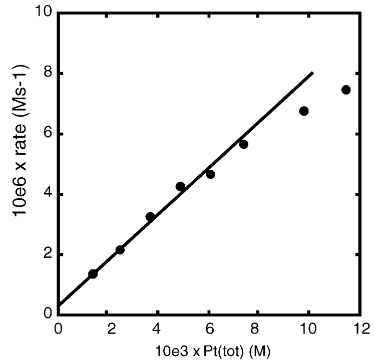


Fig. 2. Baeyer–Villiger oxidation of methylcyclohexanone with 35% hydrogen peroxide catalyzed by $[(triphosPO)Pt(CH_2Cl_2)]^{2+}$. Effect of the total Pt concentration. [2-Me-cy-one] 0.366 M; $[H_2O_2]_{org}$ 1.52×10^{-2} M; T 25 °C; N_2 1 bar.

An analysis of the effects of the concentrations of the total amount of Pt complex added, methylcyclohexanone and hydrogen peroxide is reported in Figs. 2–4. Being the system biphasic, the concentration of H_2O_2 given in the figures refers to the organic phase. It was already found [5] that the partition coefficient of hydrogen peroxide in H_2O/CH_2Cl_2 is 534/1. Therefore, the H_2O_2 concentration in the organic phase was changed by changing the concentration of the water solution, although the total amount of hydrogen peroxide used was in a 1/1 ratio with respect to the methylcyclohexanone substrate.

As can be seen from Fig. 2, the effect of total Pt concentration is first order with a negligible intercept in agreement with the observation that in the absence of

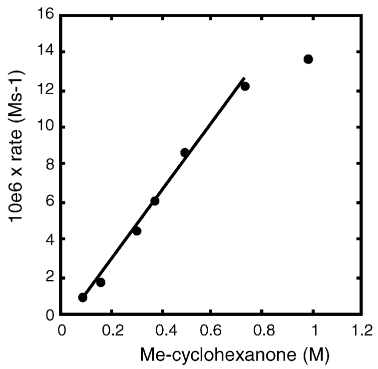


Fig. 3. Baeyer–Villiger oxidation of methylcyclohexanone with 35% hydrogen peroxide catalyzed by $[(triphosPO)Pt(CH_2Cl_2)]^{2+}$. Effect of the concentration of ketone. Pt_T 4.35×10^{-3} M; $[H_2O_2]_{org}$ 1.52×10^{-2} M; T 25 °C; N_2 1 bar.

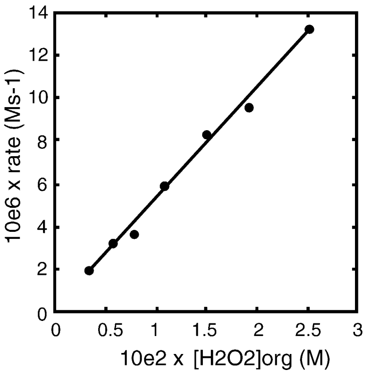


Fig. 4. Baeyer–Villiger oxidation of methylcyclohexanone with 35% hydrogen peroxide catalyzed by $[(\text{triphosPO})\text{Pt}(\text{CH}_2\text{Cl}_2)]^{2+}$. Effect of the concentration of hydrogen peroxide in the organic phase. Pt_T 4.42×10^{-3} M; [2-Me-cy-one] 0.367 M; T 25 °C; N_2 1 bar.

catalyst the reaction does not proceed. For concentrations of about $>7 \times 10^{-3}$ M a moderate levelling off starts to occur. The effect of 2-methylcyclohexanone (Fig. 3) concentration is very similar as it is first order up to about 0.8 M and then again a levelling off takes place. Finally, Fig. 4 indicates that the effect of hydrogen peroxide is first order throughout the concentration range explored.

The kinetic scheme shown in Scheme 3 is proposed, leading to the rate law indicated, where Pt_T indicates the concentration of $[(\text{P–P–O})\text{Pt}(\text{solv})]^{2+}$ initially introduced in the system and the ketone and H_2O_2 concentrations can be reasonably assumed to be the initial ones. It should be observed that Pt^{2+} as a free species is very unlikely to occur in the reaction mixture. It seems a much more realistic suggestion to assume that the fourth coordination position is occupied by any of the neutral species present in the system (i.e. dichloromethane, water, hydrogen peroxide), except the ketone.

The rate law indicated in Scheme 3 is in agreement with the effects of the reactants reported in Figs. 2–4. In fact, it fits the effect of the ketone concentration, which is first order for most of the concentration range explored and starts approaching a zero-order dependence for the maximum concentration tested. It has to be pointed out that the affinity of Pt^{2+} for ketones (i.e. the value of K in Scheme 3) must be relatively modest, as we have previously observed when studying the acidity of $[(\text{triphosPO})\text{Pt}(\text{acetone})]^{2+}$ using water as a base [2]. In fact, equilibrium (1) was studied with NMR at −70 °C in acetone d^6. These measurements indicated for the equilibrium constant a value of 1400. Although in the catalytic experiments here reported the temperature is different, as are the concentrations of free ketone and

$$[(\text{P–P–O})\text{Pt}(\text{acetone})]^{2+} + H_2O \rightleftharpoons [(\text{P–P–O})\text{Pt}(H_2O)]^{2+} + \text{acetone} \qquad (1)$$

water in CH_2Cl_2, i.e. the medium where the catalytic reaction is carried out, it seems reasonable to assume that in the latter a significant concentration of Pt(ket)^{2+} species starts building up only at high concentrations. Attempts to substantiate these observations experimentally by ^{31}P NMR were unsuccessful as at room temperature the species present are highly fluxional and no useful information can be gained.

The effect of hydrogen peroxide concentration is also in agreement with Scheme 3. The latter implies that the electrophilicity of the carbonyl carbon is increased by coordination to the Lewis acidic metal center, so that it becomes susceptible to attack even by a moderate nucleophile [6] such as hydrogen peroxide.

In principle, an alternative might be possible consisting in the increase of the neucleophilicity of hydrogen peroxide by formation of a Pt–OOH complex [7] followed by attack on the free ketone as suggested in Scheme 4. The direct reaction between $[(\text{P–P–O})\text{Pt(OOH)}]^+$ and the free ketone in CH_2Cl_2 could not be tested because, at variance with $[(\text{triphos})\text{Pt(OOH)}]^+$, the homologous species with P–P–O could not be isolated [2]. The rate law indicated in Scheme 4 is very similar to that indicated in Scheme 3, except for a dependence from the acidity of the medium. Indeed all reactions reported in Figs. 2–4 were carried out in a medium buffered at pH 1.5. To check the possible effect of acidity, a series of reactions were carried out without buffering, but adding increasing amounts of either $HClO_4$ or KOH to the aqueous phase. The corresponding effect on the initial rate of the catalytic reaction is reported in Fig. 5 and is practically negligible.

On the basis of the above experiments, kinetic Scheme 3 remains the most plausible one. However, the deviation from linearity observed at high concentrations of Pt concentration

$$\text{Pt}^{2+} + \text{ket} \overset{K}{\rightleftharpoons} \text{Pt(ket)}^{2+}$$

$$\text{Pt(ket)}^{2+} + H_2O_2 \xrightarrow[\text{rds}]{k} \text{lactone} + \text{Pt}^{2+} + H_2O$$

$$\text{in. rate} = \frac{d[\text{lactone}]}{dt} = \frac{kK\text{Pt}_\text{T}[\text{ket}][H_2O_2]}{1 + K[\text{ket}]}$$

$$\text{where } \text{Pt}^{2+} = [(\text{P-P-O})\text{Pt(solv)}]^{2+}, [(\text{P-P-O})\text{Pt}(H_2O)]^{2+}, [(\text{P-P-O})\text{Pt}(H_2O_2)]^{2+}$$
$$\text{ket} = \text{2-methylcyclohexanone}$$

Scheme 3.

$$\text{Pt}^{2+} + H_2O_2 \overset{K}{\rightleftharpoons} \text{Pt-OOH}^+ + \text{H}^+$$

$$\text{Pt-OOH}^+ + \text{ket} \xrightarrow[\text{rds}]{k} \text{lactone} + \text{Pt-OH}^+$$

$$\text{Pt-OH} + \text{H}^+ \xrightarrow{\text{fast}} \text{Pt}^{2+} + H_2O$$

$$\text{in. rate} = \frac{d[\text{lactone}]}{dt} = \frac{kK\text{Pt}_\text{T}[\text{ket}][H_2O_2]}{[\text{H}^+] + K[H_2O_2]}$$

Scheme 4.

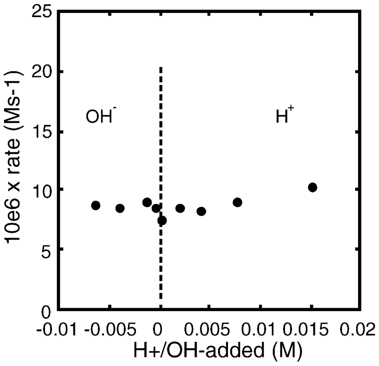
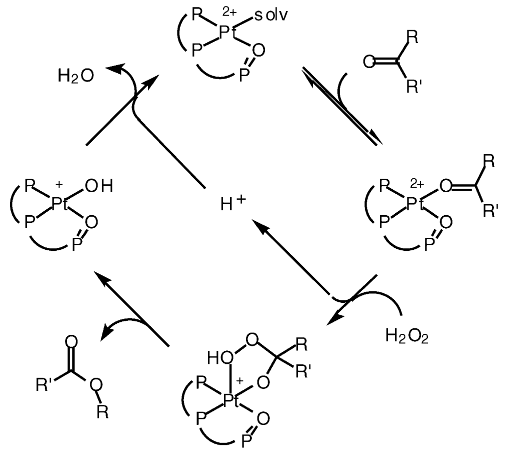


Fig. 5. Baeyer–Villiger oxidation of methylcyclohexanone with 35% hydrogen peroxide catalyzed by $[(\text{triphosPO})\text{Pt}(\text{CH}_2\text{Cl}_2)]^{2+}$. Effect of the addition of $HClO_4$ or KOH on the reaction rate. Reaction conditions: Pt_T 11.5×10^{-3} M, [ketone] 0.366 M, $[\text{H}_2\text{O}_2]_\text{org}$ 1.52×10^{-2} M.



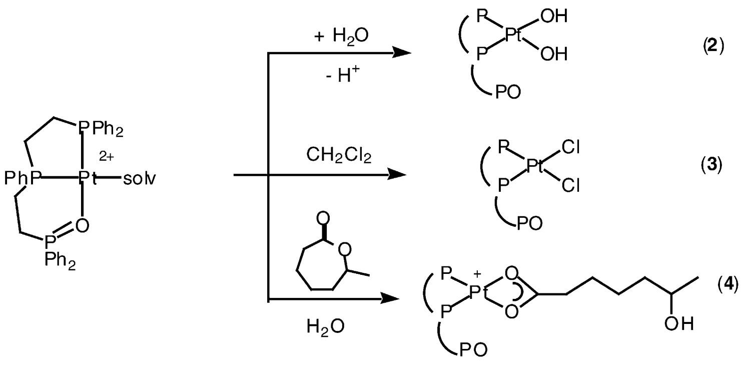
Scheme 6.

(Fig. 2) should be explained on a different ground. The most plausible rationale seems to be the existence of a side reaction subtracting active species that begins to be evident at high Pt concentrations. In Scheme 5, three possible deactivation pathways have been considered. Eq. (2) predicts the formation of a bis-hydroxo complex. This species has been previously observed and found inactive [2], but forms under basic conditions. More plausible seems the possibility of formation of the dichloro complex (Eq. (3)). Indeed, the reaction between the starting complex and CH_2Cl_2 was found [2] to deactivate the catalyst with formation of a dichloro species, but this process was observed to occur to a significant extent in boiling dichloromethane. A third possibility, depicted in Eq. (4), predicts the possible formation of an inactive carboxylato complex arising from hydrolysis of the lactone product promoted either by the acidic reaction medium, or by the Lewis acidic complex itself. The latter two possibilities would be dependent on complex concentration and would explain the effect reported in Fig. 2.

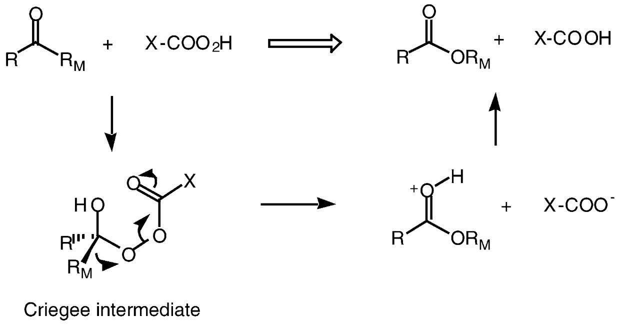
The viability of Eq. (4) was checked with a NMR experiment in which a 8×10^{-2} M solution of $[(\text{triphosPO})\text{Pt}(\text{acetone})](\text{BF}_4)_2$ in CD_2Cl_2 was reacted with two equivalents of 2-heptalactone in the presence of two equivalents of H_2O at 25 °C. The mixture was monitored for 24 h showing only the starting compound and no evidence for the formation of new species. The experiment was repeated in acetone-d^6 with identical results. Since the Pt concentration is about 10 times higher than the maximum concentration tested in the kinetic experiments, we believe that the occurrence of Eq. (4) in the catalytic system is unlikely. These results seem to suggest that the process subtracting active species to the catalytic system under (kinetically) high Pt concentrations is probably Eq. (3).

The kinetic scheme (Scheme 3) that fits better the experimental observations can be better viewed in a cyclic fashion (Scheme 6). As can be seen, the main role of the complex is to act as a Lewis acid in the activation of the carbonyl group. Moreover, after the rate determining step the formation of a *quasi*-peroxymetallacyclic intermediate is suggested, that promotes the rearrangement leading to C–C bond cleavage and insertion of the peroxy oxygen via release of a Pt–OH complex that is rapidly protonated to yield the starting compound.

As is shown in Scheme 6, the oxygen transfer is suggested to occur via a two-stage process in which the formation of a *quasi*-peroxymetallacyclic species is involved. Although species of this type have never been isolated, since the early report of Mimoun et al. [8] they have been often implied in the oxidation of unsaturated substrates [7] (see for example



Scheme 5.



Scheme 7.

[9]), including ketones [10]. Clearly, the simple kinetic analysis reported above does not distinguish between a single-stage process and a two-stage process, as the rate equation would be the same in both cases. Although not required by the rate-law, the suggestion that the rate determining step is a two-stage process has the advantage of being similar to the well-known mechanism of the stoichiometric Baeyer–Villiger oxidation using peracids [3]. It is known that this reaction proceeds (Scheme 7) through the formation of a peroxidic intermediate, the so-called "Criegee intermediate" [11] (which bears strong similarities with the *quasi*-peroxyplatinacyclic intermediate involved in Scheme 6) from which the ester product forms via a simple rearrangement. Of the two stages, the second is generally considered to be rate determining [3d,f], as this is in agreement with both the order of reactivity of different peracids (which parallels the properties of X–COO− as a leaving group) and the order of migratory aptitude for different alkyl (aryl) groups. This view suggests also a further important role for Pt in the reaction, i.e. the assistance given by the metal center to the dissociation of HO^- (per se a bad leaving group) from the peroxyplatinacyclic intermediate, thus making hydrogen peroxide a valuable oxidant for the reaction.

3. Conclusions

The kinetic study on the catalyzed Baeyer–Villiger oxidation of ketones with hydrogen peroxide confirms the reactivity studies reported in a previous paper on the importance of the Lewis acidity of the catalyst as an important parameter to be exploited in designing new catalytic systems capable to promote this synthetically very useful, but otherwise catalytically elusive reaction. As we have already observed [2], Lewis acidity is also the key to direct the selectivity to the Baeyer–Villiger oxidation with respect to other possible oxidation processes, namely epoxidation. Indeed, the class of (phosphine)Pt complexes reported here and elsewhere [2,10] are probably the best catalysts for the Baeyer–Villiger oxidation of ketones. They show TON and TOF as high as 330 and 10^5 h^{-1}, respectively, in the case of cyclobutanone [10a,b], they can oxidize open chain ketones [10e], they can be easily modified to carry out enantioselective reactions [10c,f]. This versatility makes them better than Cu(II) (see for example [12]), Al(III) [13] or even heterogeneous Sn(IV) [14] systems that are in principle better Lewis acids. This is most probably due to the combination of Lewis acidity and ability to promote the leaving of HO^- which appears to be a unique property of Pt systems.

4. Experimental section

4.1. Apparatus

IR spectra were taken on a Nicolet 750 spectrophotometer either in nujol mulls using KBr plates or in CH_2Cl_2 solution using CaF_2 windows. $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded on a Bruker AC200 spectrometer operating in FT mode, using as external reference 85% H_3PO_4 and TMS, respectively. Negative chemical shifts are upfield from the reference. GLC measurements were taken on a Hewlett-Packard 5890A gas chromatograph equipped with a FID detector (gas carrier He). Identification of products was made with GLC by comparison with authentic samples.

4.2. Materials

Solvents were dried and purified according to standard methods. Substrates were purified by passing through neutral allumina and stored in the dark at low temperature. Hydrogen peroxide (35% Fluka), triphos (Aldrich), HBF_4 54% in ether (Aldrich) were commercial products and used without purification.

The complex $[(\text{triphosPO})Pt(CH_2Cl_2)](BF_4)_2$ used as catalyst was prepared according to Ref. [2].

4.3. Kinetic studies

These were carried out in a 10 ml round-bottomed flask equipped with a stopcock for vacuum/N_2 operations and a sidearm fitted with a screw-capped silicone septum to allow sampling. Stirring was performed by a teflon-coated bar driven externally by a magnetic stirrer. Constant temperature (20 ± 0.1 °C) was maintained by water circulation through an external jacket connected with a thermostat. Absence of diffusional problems was determined by the conversion versus time plots independence of the stirring rate in randomly selected catalytic experiments. The concentration of the commercial 35% H_2O_2 solution was checked iodometrically prior to use.

The following general procedure was followed: the required amount of catalyst was placed in solid form in the reactor, which was evacuated and filled with N_2. Purified, N_2-saturated 2-methylcyclohexanone was added under N_2 flow, followed by the required amount of dichloromethane.

After thermostating at the required temperature for a few minutes, the H_2O_2 solution in the appropriate amount was injected through the septum and time was started.

All reactions were monitored with GLC by direct injection of samples taken periodically from the reaction mixtures with a microsyringe. Prior quenching of the samples by adding an excess of LiCl was found unnecessary. Initial rate data were determined from conversion versus time plots. Separation of the products was performed on a 25 m HP-5 capillary column using a flame ionization detector.

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References

[1] (a) G. Strukul, Top. Catal. 19 (2002) 33;
 (b) K. Hori, J. Ito, T. Ohta, I. Furukawa, Tetrahedron 54 (1998) 12737;
 (c) D. Ferraris, B. Young, T. Dudding, T. Lectka, J. Am. Chem. Soc. 120 (1998) 4548;
 (d) A.K. Ghosh, H. Matsuda, Org. Lett. 1 (1999) 2157;
 (e) S. Oi, E. Terada, K. Ohuchi, T. Kato, Y. Tachibana, I. Inoue, J. Org. Chem. 64 (1999) 8660;
 (f) K. Hori, H. Kodama, T. Ohta, I. Furukawa, J. Org. Chem. 64 (1999) 5017;
 (g) K. Pignat, J. Vallotto, F. Pinna, G. Strukul, Organometallics 19 (2000) 5160;
 (h) J. Hao, M. Hatano, K. Mikami, Org. Lett. 2 (2000) 4059;
 (i) T. Hattori, Y. Suzuki, O. Uesugi, S. Oi, S. Miyana, Chem. Commun. (2000) 73;
 (j) A. Fürstner, D. Voigtländer, W. Schrader, D. Giebel, M. Reetz, Org. Lett. 3 (2001) 417;
 (k) N.M. Brunkan, P.S. White, M.R. Gagné, Organometallics 21 (2002) 1565;
 (l) N.M. Brunkan, M.R. Gagné, Organometallics 21 (2002) 1576.
[2] A. Brunetta, G. Strukul, Eur. J. Inorg. Chem. (2004) 1030.
[3] (a) C.H. Hassall, React. Org. 9 (1957) 73;
 (b) J.E. Leffler, Chem. Rev. 45 (1949) 385;
 (c) J.B. Lee, B.C. Uff, Quart. Rev. (London) 21 (1967) 429;
 (d) H.O. House, Modern Synthetic Reactions, Benjamin, New York, 1972;
 (e) B. Plesnicar, in: W.S. Trahanovsky (Ed.), Oxidation in Organic Chemistry, Part C, Academic Press, New York, 1978, p. 254;
 (f) M. Hudlicky, Oxidations in Organic Chemistry, American Chemical Society, Washington, 1990;
 (g) G.C. Krow, Org. React. 43 (1993) 251.
[4] (a) G. Strukul, Angew. Chem. Int. Ed. Engl. 37 (1998) 1198;
 (b) G. Strukul, Nature 412 (2001) 388, and references therein.
[5] Zanardo, F. Pinna, Michelin R.A., G. Strukul, Inorg. Chem. 27 (1988) 1966.
[6] C.W. Jones, Applications of Hydrogen Peroxide and Derivatives, The Royal Society of Chemistry, Cambridge, 1999.
[7] G. Strukul (Ed.), Catalytic Oxidations with Hydrogen Peroxide as Oxidant, Kluwer Academic Publishers, Dordrecht, 1992(Chapter 6).
[8] H. Mimoun, R. Charpentier, A. Mitschler, J. Fischer, R. Weiss, J. Am. Chem. Soc. 102 (1980) 1047.
[9] (a) H. Mimoun, in: G. Wilkinson, R.D. Gillard, J. McCleverty (Eds.), Comprehensive Coordination Chemistry, Pergamon Press, Oxford, 1987, p. 317, Chapter 61.3;
 (b) K.A. Jørgensen, Chem. Rev. 89 (1989) 431.
[10] (a) M. Del Todesco Frisone, F. Pinna, G. Strukul, Stud. Surf. Sci. Catal. 66 (1991) 405;
 (b) M. Del Todesco Frisone, F. Pinna, G. Strukul, Organometallics 12 (1993) 148;
 (c) A. Gusso, C. Baccin, F. Pinna, G. Strukul, Organometallics 13 (1994) 3442;
 (d) G. Strukul, A. Varagnolo, F. Pinna, J. Mol. Catal. 117 (1997) 413;
 (e) R. Gavagnin, M. Cataldo, F. Pinna, G. Strukul, Organometallics 17 (1998) 661;
 (f) C. Paneghetti, R. Gavagnin, F. Pinna, G. Strukul, Organometallics 18 (1999) 5056.
[11] R. Criegee, Justus Liebigs Ann. Chem. 560 (1948) 127.
[12] (a) C. Bolm, G. Schlingloff, K. Weickardt, Angew. Chem. Int. Ed. 33 (1994) 1848;
 (b) C. Bolm, G. Schlingloff, Chem. Commun. (1995) 1247.
[13] C. Bolm, O. Beckmann, C. Palazzi, Can. J. Chem. 79 (2001) 1593.
[14] L.T. Corma, M. Nemeth, S. Renz, Valencia, Nature 412 (2001) 423.