

Chromium(VI)-Catalyzed Oxidations by Hydrogen Peroxide: Influence of the Presence of Water and Base[☆]

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The chromium(VI)-catalyzed oxidation of 1-indanol into 1-indanone has been carried out with sodium percarbonate (SPC), urea-hydrogen peroxide adduct (UHP), or aqueous hydrogen peroxide. It has been established that the

superiority of SPC over UHP and aqueous H₂O₂ is due both to its nonhydrated structure and its basic properties. This classifies SPC as a "dry basic carrier of H₂O₂".

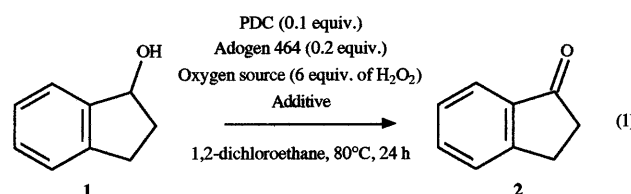
Introduction

Oxidation reactions are important transformations in organic synthesis^[1]. Economic and environmental constraints are strong incentives for replacing stoichiometric procedures by catalytic ones with inexpensive oxygen sources. Over the last twelve years, our group has been intensively involved in chromium(VI)-catalyzed oxidations with *tert*-butyl hydroperoxide (TBHP)^[2]. Although TBHP is readily available, it would be more advantageous to use hydrogen peroxide rather than TBHP, because it is cheaper and the by-product is merely water instead of *tert*-butanol.

The chromium(VI)-catalyzed oxidation of the benzylic methylene group of alkylarenes by TBHP is not greatly influenced by the water content of the oxygen source since fair conversions and yields have been obtained with aqueous and anhydrous solutions of TBHP^[3]. In contrast, the replacement of commercial aqueous 70% TBHP by commercial aqueous 30% H₂O₂^{[3b][3c][3d]} is strongly detrimental to the efficiency of the reaction. Switching from aqueous 30% H₂O₂ to commercial anhydrous hydrogen peroxide-adducts such as urea-hydrogen peroxide (H₂NCONH₂·H₂O₂ = UHP)^{[3d][4][5]} or in particular sodium percarbonate (Na₂CO₃·1.5 H₂O₂ = SPC)^[6] improves the transformation. We have also remarked that the yields of the chromium(VI)-catalyzed oxidations of alcohols by anhydrous TBHP^[3f], aqueous 70% TBHP^[7], or SPC^[8] are often similar^[9]. These observations are of great value since SPC is produced on a large scale at low price, for use mainly in the detergent industry as a bleaching or antiseptic agent^[10]. SPC is beginning to emerge as an effective reagent in organic synthesis but, heretofore, it has rarely been employed in the presence of metal catalysts^{[11][12]}.

We now report that SPC also gives better results than aqueous H₂O₂ and UHP in the chromium(VI)-catalyzed oxidation of alcohols. Results obtained under selected conditions (Eq. 1, Table 1) led us to determine the factors

which play a role in the relative efficiencies of these three sources of hydrogen peroxide. The model reaction was the oxidation of 1-indanol (**1**) into 1-indanone (**2**) with 1,2-dichloroethane as solvent and a mixture of pyridinium dichromate (PDC)^[13] and Adogen 464^[14] as catalyst. The main role of Adogen 464 is to interact with PDC to form a chromium complex which is soluble in 1,2-dichloroethane^[15].



Results and Discussion

The experimental conditions used as reference were those previously documented: 4 equiv. of SPC and catalytic amounts of both PDC and Adogen 464 in 1,2-dichloroethane at reflux for 24 h (Table 1, run 1)^[8a]. To obtain valid comparisons, the same quantity of hydrogen peroxide was used in all runs; owing to the formula of SPC, that implied 6 equiv. of aqueous H₂O₂ or UHP.

Replacing SPC by aqueous H₂O₂ led to a dramatic decrease in the conversion of **1** and to a lower selectivity for **2** (run 2). Therefore, to aqueous H₂O₂ we added a quantity of sodium carbonate identical to the one contained above in SPC; this improved the results (run 3) but they remained inferior to those obtained with anhydrous SPC. When a quantity of H₂O equivalent to (run 4) or slightly more than (run 5) the water content of aqueous H₂O₂ was added to SPC, the efficiency of the oxidation was similar to that obtained with aqueous H₂O₂/Na₂CO₃ (run 3). From these re-

Table 1. PDC-catalyzed oxidation of indan-1-ol to indan-1-one by various forms of hydrogen peroxide^[a]

Runs	Oxygen source (mmol)	Additive (mmol)	Conversion %	Isolated yield %	Selectivity % ^[b]
1	SPC (4)	(0)	86	84	98
2	Aqueous 35% H ₂ O ₂ (6)	(0)	49	40	82
3	Aqueous 35% H ₂ O ₂ (6)	Na ₂ CO ₃ (4)	58	50	86
4	SPC (4)	H ₂ O (21)	65	60	92
5	SPC (4)	H ₂ O (29)	56	46	82
6	UHP (6)	(0)	65	64	98
7	UHP (6)	Na ₂ CO ₃ (4)	87	83	96
8	UHP (6)	H ₂ O (21)	53	45	85
9	UHP (6)	Na ₂ CO ₃ (4) + H ₂ O (21)	51	47	91
10	UHP (6)	Na ₂ SO ₄ (4)	47	40	85
11	UHP (6)	MgSO ₄ (4)	34	31	91
12	UHP (6)	CaCl ₂ (4)	38	25	66
13	UHP (6)	Na ₂ CO ₃ (1)	25	24	96

^[a] Conditions: 1-indanol (1 mmol), PDC (0.1 mmol), Adogen 464 (0.2 mmol), free or associated H₂O₂ (6 mmol), additive (0–29 mmol), 1,2-dichloroethane (10 ml), 80°C, 24 h, air atmosphere. – ^[b] Selectivity represents the yield based on the amount of substrate consumed.

sults, it appears that the presence of sodium carbonate is beneficial to the process while that of water is prejudicial.

The detrimental role of water in the present process^[16] could be attributed to its competition with H₂O₂ and/or **1** in coordination to the active chromium species^[17]. As for sodium carbonate, it could either act as a desiccant of the mixture^[18] or through its basic properties.

To obtain more accurate conclusions, the oxidation of **1** was next carried out with UHP. A clean oxidation was thus observed but the conversion was only 65% (run 6). This latter increased to 87% when Na₂CO₃ was used as additive (run 7); the results were therefore similar to those obtained with commercial SPC (run 1). As anticipated, the addition of water to UHP led to less effective experimental conditions (runs 8 and 9); conversions and yields were on the same order as those afforded by aqueous H₂O₂ (runs 2 and 3). These observations are in agreement with the above hypothesis regarding the role of water. Moreover, they show that the urea contained in UHP has no effect on the course of the process.

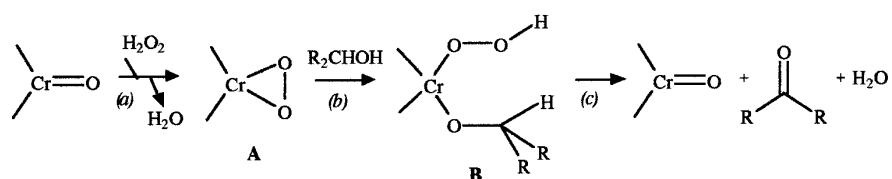
A by-product common to the oxidations with the different sources of hydrogen peroxide is water which could be removed from the organic phase by combining with Na₂CO₃^[18]. Since the oxidation reaction is carried out at 80°C, we presumed that the hydrated form of Na₂CO₃ would be rather unstable at this temperature^[18]. So, this salt was exchanged for stronger drying agents such as Na₂SO₄, MgSO₄, and CaCl₂^[18] (runs 10 to 12). In their presence, the oxidation with UHP was, however, less effective than with Na₂CO₃ (run 7) and even than in their absence (run 6).

From the latter experiments, it appears that the role of Na₂CO₃ is more likely due to its basic properties. Literature reports^{[11][19][20][21][22][23]} suggest that these can interfere in the oxidation mixture at various stages as described below.

The decomposition of H₂O₂ was known to be i) catalyzed by traces of many transition metals, and ii) extremely slow in aqueous alkaline media^[19]. It was of interest to note that in alkaline solutions, a slow catalytic decomposition has been reported even for chromium(VI)/H₂O₂ mixtures^[20]. Therefore, the H₂O₂ content of the crude mixtures obtained from runs 1 and 2 was determined by iodometry; that gave 0.12 mmol of H₂O₂ for the former and 0.03 mmol of H₂O₂ for the latter. From these slight differences, it appears that the large drop in the conversion in the absence of a basic medium is not mainly due to the unproductive destruction of H₂O₂ leading to a failure of the oxidant.

Mono-, di-, tri-, and tetraperoxochromium complexes have been characterized from the reaction of chromium(VI) oxides and H₂O₂^{[20][22][24]}; some oxodiperoxochromium(VI) compounds have been used for various stoichiometric oxidations including those of alcohols^[25]. This led us to envisage peroxochromium species such as **A** as intermediates in the reactions of the present report (Scheme 1); their formation could be facilitated by the generation of HOO[–] from H₂O₂^{[11][21]} in the presence of base. The addition of SPC to the dark-orange colored PDC/Adogen 464 solution immediately produced a red-brown colored mixture, indicating the formation of tetraperoxochromium species^[26]. On the addition of aqueous H₂O₂ instead of SPC, the color change was also instantaneous but led to a deep-blue solution indi-

Scheme 1



cating the formation of a different peroxo species. These differences are in agreement with literature data, since it has been shown that the nature and the stability of the peroxochromium species formed from oxochromium and H_2O_2 depends strongly on the pH^{[20][22][27]}. It has also been suggested that the catalytic activity of peroxochromium species in the decomposition of H_2O_2 depends highly on the number of peroxo groups coordinated to chromium: inactive with two or four groups, active with one or three groups^[20]. Nevertheless, this does not imply that the same pattern of reactivity would be necessarily followed for peroxochromium-catalyzed oxidations with H_2O_2 . In fact, a literature survey led us to find only one such report regarding a catalytic reaction: the allylic oxidation of cyclohexene by H_2O_2 with an oxodiperoxochromium(VI) compound as starting catalyst, albeit with a low turnover number^{[25d][29]}. The interreactions of chromium with H_2O_2 are exceptionally complicated^{[20][22][24b]}; even if a complex is well characterized, it is not necessarily the real catalyst^[29].

In addition, Na_2CO_3 could enhance the nucleophilicity of the alcohol and even possibly give the corresponding sodium alkoxide as assumed for some metal-catalyzed oxidations^{[23a][23c]}. This would promote the formation of hydroperoxochromium alkoxide **B** (Scheme 1, path *b*).

The base could also mediate the termination of the catalytic cycle (path *c*) in abstracting the hydrogen geminal to the chromiumalkoxy group of **B** as postulated for a similar molybdenum catalyst^[23b].

According to the mechanism depicted in Scheme 1 and the above remarks, a catalytic amount of base could be sufficient. Relative to run 7, a reaction carried out with UHP and a lower quantity of Na_2CO_3 however afforded inferior results (run 13).

From these studies, it appears that the base could play several roles. On the whole, its presence serves to increase the efficiency of the reaction without leading to significant amounts of side-products.

Conclusion

The superiority of SPC over both aqueous H_2O_2 and UHP for the chromium(VI)-catalyzed oxidation of alcohols is due to both its non-hydrated structure and its basic properties. Consequently, SPC which has already been considered as a "solid form"^[10c] or a "portable form"^{[30][31]} of H_2O_2 is indeed rather best looked at as a "dry basic carrier of H_2O_2 ".

Aqueous H_2O_2 has been used for more than half a century^{[2a][32]} for various oxidations catalyzed not only by chromium oxides but also by a number of other transition-metal salts and complexes^[33]. The efficiency of some procedures is limited by the large amount of water introduced. Therefore, the potential scope of SPC – an inexpensive bulk chemical – could be wide.

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Experimental Section

Reagents and substrate are commercially available and were used as received. – Home-made plates (silica gel 60 PF₂₅₄ + 366 from Merck) were used for preparative thin-layer chromatography.

WARNING: Hydroperoxides present an explosion hazard in the presence of transition-metal salts or when concentrated or heated^{[5][34]}. Safety precautions have to be followed especially in large-scale reactions. So, a reductive workup^{[34][35]} has to be carried out to remove residual peroxides.

General Oxidation Procedure: Into a 25-ml round-bottomed flask were placed sequentially PDC (38 mg, 0.1 mmol), Adogen 464 (81 mg, A 0.2 mmol), 1,2-dichloroethane (10 ml), oxidant (SPC: 628 mg, 4 mmol, aqueous 35% H_2O_2 : 583 mg, 6 mmol or UHP: 564 mg, 6 mmol), additives (0–29 mmol, see Table 1), and 1-indanol (134 mg, 1 mmol). The mixture was stirred and refluxed under an air atmosphere for 24 h. After cooling to room temperature, the slurry was filtered. The filtrate was evaporated to dryness at room temperature under reduced pressure. Unreacted 1-indanol and 1-indanone were isolated by preparative thin-layer chromatography of the residue, eluting with EtOAc/petroleum ether (10:90).

Remark: To obtain reproducible results, it is necessary to wait for the complete dissolution of PDC (formation of a soluble chromium complex by exchange of the ammonium groups between PDC and Adogen 464)^[15] before carrying out the subsequent additions.

Iodometric Titration: Water (5 ml) was added to the crude mixture. After stirring for 5 min, the aqueous phase was recovered. Its iodometric titration was carried out as described in ref.^[35].

☆ Dedicated to Prof. *E. J. Corey* on the occasion of his 70th birthday.

- [1] [1a] G. Cainelli, G. Cardillo, *Chromium Oxidations in Organic Chemistry*, Springer-Verlag: Berlin, **1984**. – [1b] A. H. Haines, *Methods for the Oxidation of Organic Compounds*, Acad. Press: London, **1985** and **1988**. – [1c] *Organic Syntheses by Oxidation with Metal Compounds*, (Eds.: W. J. Mijs, C. R. H. I. De Jonge), Plenum Press: New York, **1986**.
- [2] For reviews including parts of our studies: [2a] J. Muzart, *Chem. Rev.* **1992**, 92, 113–140. – [2b] J. Muzart, *Synthesis* **1993**, 11–27.
- [3] [3a] J. Muzart, *Tetrahedron Lett.* **1986**, 27, 3139–3142. – [3b] J. Muzart, *Tetrahedron Lett.* **1987**, 28, 2131–2132. – [3c] J. Muzart, A. N'Ait Ajjou, *J. Mol. Catal.* **1991**, 66, 155–161. – [3d] J. Muzart, A. N'Ait Ajjou, G. V. Nizova, G. B. Shul'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1991**, 1454–1457; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1991**, 40, 1294–1296. – [3e] J. Muzart, A. N'Ait Ajjou, *Synth. Commun.* **1993**, 23, 2113–2118. – [3f] J. Muzart, *Synth. Commun.* **1989**, 19, 2061–2067.
- [4] For the advantages of UHP as a source of H_2O_2 : R. W. Murray, K. Iyanar, *J. Org. Chem.* **1998**, 63, 1730–1731 and references included.
- [5] For precautions in the use of UHP: M. S. Cooper, H. Heaney, A. J. Newbold, W. R. Sanderson, *Synlett* **1990**, 533–535.
- [6] J. Muzart, S. Ait-Mohand, *Tetrahedron Lett.* **1995**, 36, 5735–5736.
- [7] [7a] J. Muzart, *Tetrahedron Lett.* **1987**, 28, 2133–2134. – [7b] J. Muzart, A. N'Ait Ajjou, *Synthesis* **1993**, 785–787. – [7c] A. N'Ait Ajjou, J. Muzart, L. Savelon, G. Guillaumet, *Synthesis* **1994**, 359–360.
- [8] [8a] J. Muzart, A. N'Ait Ajjou, S. Ait-Mohand, *Tetrahedron Lett.* **1994**, 35, 1989–1990. – [8b] S. Ait-Mohand, J. Muzart, *Synth. Commun.* **1995**, 25, 2373–2377.
- [9] The chromium(VI)-catalyzed oxidation of alcohols by aqueous 30% H_2O_2 has been observed but no yield was reported: S. Kanemoto, S. Matsubara, K. Takai, K. Oshima, K. Utimoto, H. Nozaki, *Bull. Chem. Soc. Jpn.* **1988**, 61, 3607–3612.
- [10] [10a] J. Rémond, *Rev. Prod. Chim.* **1954**, 57, 401–404. – [10b] J. Rémond, *Rev. Prod. Chim.* **1954**, 57, 451–454. – [10c] Chem. Eng. News **1980**, 58 (July 21), 39–40. – [10d] T. K. Das, A. K. Mandavawalla, S. K. Datta, *Colourage* **1983**, 30 (26), 15–21.

- [11] For reviews on the use of SPC in organic synthesis: [11a] A. McKillop, W. R. Sanderson, *Tetrahedron* **1995**, *51*, 6145–6166. — [11b] J. Muzart, *Synthesis* **1995**, 1325–1347.
- [12] For recent reports concerning SPC and metal catalysis: [12a] Refs. [7][9][13], — [12b] S. Aït-Mohand, A. Levina, J. Muzart, *Synth. Commun.* **1995**, *25*, 2051–2059. — [12c] S. Aït-Mohand, A. Levina, S. Lunak, J. Muzart, *Inorg. Chim. Acta* **1995**, *238*, 183–185. — [12d] S. Aït-Mohand, S. Lunak, J. Muzart, *Chem. Ber.* **1997**, *130*, 1655–1658 and references included. — [12e] C. W. Jones, A. Hackett, I. Pattinson, A. Johnstone, S. L. Wilson, *J. Chem. Res. (S)* **1996**, 438–439; *J. Chem. Res. (M)* **1996**, 2501–2525. — [12f] A. Sorokin, L. Fraisse, A. Rabion, B. Meunier, *J. Mol. Catal. A: Chem.* **1997**, *117*, 103–114.
- [13] E. J. Corey, G. Schmidt, *Tetrahedron Lett.* **1979**, 399–402.
- [14] Adogen 464 is a registered trademark of Ashland Chemical Co. for methyltrialkyl(C₈–C₁₀)ammonium chloride.
- [15] J. Muzart, S. Aït-Mohand, *New. J. Chem.* **1995**, *19*, 207–211.
- [16] For other examples: G. Strukul in *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, (Ed.: G. Strukul); Kluwer Acad. Pub.: Dordrecht, **1992**, pp 1–11.
- [17] R. A. Sheldon, *J. Mol. Catal.* **1980**, *7*, 107–126.
- [18] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals* Pergamon Press: London, **1966**.
- [19] E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun, J. O. Edwards, *J. Am. Chem. Soc.* **1963**, *85*, 2263–2268.
- [20] S. B. Brown, P. Jones, A. Suggett, *Prog. Inorg. Chem.* **1970**, *13*, 159–204.
- [21] R. Curci, J. O. Edwards in *Catalytic Oxidations with Hydrogen Peroxide as Oxidant* (Ed.: G. Strukul); Kluwer Acad. Pub.: Dordrecht, **1992**, pp 45–95.
- [22] M. H. Dickman, M. T. Pope, *Chem. Rev.* **1994**, *94*, 569–584.
- [23] [23a] Y. Tamaru, Y. Yamada, K. Inoue, Y. Yamamoto, Z. Yoshida, *J. Org. Chem.* **1983**, *48*, 1286–1292. — [23b] B. M. Trost, Y. Masuyama, *Tetrahedron Lett.* **1984**, *25*, 173–176. — [23c] M. L. S. Almeida, M. Beller, G.-Z. Wang, J.-E. Bäckvall, *Chem. Eur. J.* **1996**, *48*, 1533–1536. — [23d] K. P. Peterson, R. C. Larock, *J. Org. Chem.* **1998**, *63*, 3185–3189.
- [24] [24a] R. Stomberg, I. B. Ainalem, *Acta Chem. Scand.* **1968**, *22*, 1439–1451. — [24b] L. Zhang, P. A. Lay, *Inorg. Chem.* **1998**, *37*, 1729–1733.
- [25] [25a] J. E. Baldwin, J. C. Swallow, H. W. S. Chan, *Chem. Commun.* **1971**, 1407–1408. — [25b] G. W. J. Fleet, W. Little, *Tetrahedron Lett.* **1977**, 3749–3750. — [25c] J. Drabowicz, *Synthesis* **1980**, 125–126. — [25d] E. Daire, H. Mimoun, L. Saussine, *New. J. Chem.* **1984**, *8*, 271–274. — [25e] H. Firouzabadi, N. Iranpoor, F. Kiaeezadeh, J. Toofan, *Tetrahedron* **1986**, *42*, 719–725. — [25f] B. Tamami, H. Yeganeh, *Tetrahedron* **1997**, *53*, 7889–7896.
- [26] J. W. Peters, J. N. Pitts, I. Rosenthal, H. Fuhr, *J. Am. Chem. Soc.* **1972**, *94*, 4348–4350.
- [27] The blue perchromic acid obtained from the addition of HP to an acidic solution of potassium dichromate was observed as far back as 1843^[28]. Investigations concerning the structure of the peroxochromium species has led to considerable controversy^{[2a][20][22]}. The blue color is preserved in the presence of pyridines^{[25b][25d][25e]} and pyrazines^[25f] while red-brown tetra-peroxochromium species are formed in alkaline solutions^{[20][26]}.
- [28] L. C. Barreswil, *C. R. Acad. Sci. Paris* **1843**, *16*, 1085–1087.
- [29] [29a] In Mimoun's study^[25d], it has not been established whether the initial complex - (Ph₃PO)O=Cr(O₂)₂ - was involved in the catalytic cycle. — [29b] See also ref.^[9].
- [30] M. A. A. F. de C. T. Carrondo, W. P. Griffith, D. P. Jones, A. C. Skapski, *J. Chem. Soc., Dalton Trans.* **1977**, 2323–2327.
- [31] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd ed., Wiley, New York, **1982**, vol. 17, p. 6. — [31b] Kirk-Othmer *Encyclopedia of Chemical Technology*, 3rd ed., Wiley: New York, **1982**, vol. 17, p. 6.
- [32] N. A. Milas, *J. Am. Chem. Soc.* **1937**, *59*, 2342–2344.
- [33] [33a] R. A. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds* Acad. Press: New York, **1981**. — [33b] Y. Ogata, Y. Sawaki in ref.^[1c], pp 839–876. — [33c] J. O. Edwards, R. Curci, B. Meunier, G. Strukul, V. Conté, F. Di Furia, C. L. Hill in *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, (Ed.: G. Strukul); Kluwer Acad. Pub.: Dordrecht, **1992**, pp 97–280.
- [34] K. B. Sharpless, T. R. Verhoeven, *Aldrichimica Acta* **1979**, *12*, 63–74.
- [35] A. M. D'A Rocha-Gonsalves, R. A. W. Johnstone, M. M. Pereira, J. Shaw, *J. Chem. Res. (S)* **1991**, 208–209; *J. Chem. Res. (M)* **1991**, 2101–2118.

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