BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (1), 188—191 (1978) [Vol. 51, No. 1

Autoxidation Reactions of Hydrocarbons Catalyzed by Co(II) Tetra(*p*-tolyl)porphyrin

Yasukazu OHKATSU and Teiji TSURUTA

Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received April 25, 1977)

Autoxidation reactions of saturated and unsaturated hydrocarbons were carried out using Co(II) tetra(*p*-tolyl)porphyrin as the catalyst in ethyl acetate at 30 °C. The Co(II) complex activated the oxygen molecule to the superoxide ion, which abstracted a hydrogen atom from a saturated hydrocarbon or added to the double bond of an unsaturated hydrocarbon, to initiate autoxidation. The reactivity of the activated oxygen molecule was found at the site of the free radical rather than that of the anion thereof. The reactivities were compared with those of superoxide ions derived from other origins.

The superoxide ion is known to be formed by several different methods: the electroreduction of molecular oxygen,[1,2] the activation of molecular oxygen on some organometallic complexes.[3] and the complexation of the potassium cation of KO_2 with crown ethers.[4]

The superoxide ion is considered to have dual characteristics as a free radical and also as an anion. For example, the electrogenerated free superoxide ion is known[1] to oxidize organic substrates according to the two mechanisms mentioned above. The superoxide ion originating from KO_2, on the other hand, behaves as an anion, as may be seen in the nucleophilic oxidation of alkyl halide to form dialkyl peroxide.[5] Little information, however, has been available on the nature of the molecular oxygen which is activated on a metal complex, especially on a metal porphyrin, though the metal complex is known to catalyze the autoxidation reaction of aldehydes.[6,7]

The purpose of this paper is to elucidate the reactivity of molecular oxygen activated on Co(II) tetra(*p*-tolyl)porphyrin in autoxidation reactions of several hydrocarbons, and to compare the reactivity with that of superoxide ions resulting from other sources.

Experimental

Materials. Co(II) tetra(*p*-tolyl)porphyrin (reffered to as CoTPP) was prepared, according to the method described by Rothemund *et al.*,[8] from pyrrole, *p*-tolualdehyde, and cobalt(II) acetate.

The hydrocarbons, such as tetralin, cumene, 2-norbornene, *dl*-limonene, cyclopentene, cyclohexene, 1-methylcyclohexene, 4-methylcyclohexene, 1,3-dihydrohexadiene, cycloheptene, cyclooctene, and cyclodecene, were purified by conventional methods using activated alumina. The furan, 2,5-dihydrofuran, and 2,3-dihydropyran were used after simple distillations.

The ethyl acetate used as a solvent and the 1,1′-azobiscyclohexanecarbonitrile used as an initiator were purified by usual methods.

Procedure. The autoxidation of a hydrocarbon was carreid out as has been described in a previous paper.[6] The $k_p/(2k_t)^{1/2}$ value was determined with 1,1′-azo-biscyclohexanecarbonitrile under the irradiation of a high-voltage mercury lamp. The rates of chain initiation were determined by the usual induction-period method, using 2,6-di-*t*-butyl-4-methylphenol as the inhibitor. The oxidation products for the two hydrocarbons were analyzed by means of GLC method (column: Silicone SE-1, column temperature: 100 °C) using authentic samples.

Results and Discussion

Autoxidation of Hydrocarbons. It is widely accepted that the autoxidation reactions of organic compounds proceed through the following steps:

$$\mathrm{RH} \longrightarrow \mathrm{R}\cdot \ (\text{or } \dot{\mathrm{R}}\mathrm{H}) \ \text{rate: } R_i, \tag{1}$$

$$\mathrm{R}\cdot + \mathrm{O_2} \longrightarrow \mathrm{RO_2}\cdot \ (\text{or } \dot{\mathrm{R}}\mathrm{H} + \mathrm{O_2} \longrightarrow \mathrm{HROO}\cdot), \tag{2}$$

$$\mathrm{RH} + \mathrm{RO_2}\cdot \xrightarrow{k_p} \mathrm{RO_2H} + \mathrm{R}\cdot \quad (\text{or } \mathrm{RH} + \mathrm{HROO}\cdot \xrightarrow{k_p} \mathrm{HROO\dot{R}H}), \tag{3}$$

$$2(\text{peroxyl radical}) \xrightarrow{k_t} \text{inert compounds}, \tag{4}$$

provided that the chain length is sufficiently long and the partial pressure of oxygen is high. The rate of oxidation is expressed[9] as

$$R = -\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = \{k_p/(2k_t)^{1/2}\}[\mathrm{RH}]R_i^{1/2}. \tag{5}$$

Cobalt(II) tetra(*p*-tolyl)porphyrin was recently shown[6] to behave as a catalyst which initiates the autoxidation of acetaldehyde by activating molecular oxygen into the superoxide type; the rate of initiation reaction was expressed as

$$R_i = k_i[\mathrm{CH_3CHO}][\mathrm{CoTPP}][\mathrm{O_2}]. \tag{6}$$

The present study has revealed that hydrocarbons also undergo the autoxidation reaction with the aid of Co(II) tetra(*p*-tolyl)porphyrin as a catalyst. Tables 1 and 2 show the results of the autoxidation reactions of the two representatitave hydrocarbons, cyclohexene, and 2,3-dihydrofuran respectively. The data in Tables 1 and 2 can satisfactorily be expressed by

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = \mathrm{const}[\mathrm{RH}]^{3/2}[\mathrm{CoTPP}]^{1/2}[\mathrm{O}]_2^{1/2}. \tag{7}^{*}$$

By comparing Eq. 7 with Eq. 5, it may be seen that the rate of initiation possesses the formula,

$$R_i = (2k_t)\left(\frac{\mathrm{const}}{k_t}\right)^2[\mathrm{RH}][\mathrm{CoTPP}][\mathrm{O_2}]. \tag{8}$$

Eq. 8 is exactly the same type as that found in the autoxidation of acetaldehyde catalyzed by the same catalyst.[6] The kinetic results are compatible with the concept that the autoxidations of cyclohexene and

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* The term "const" in Eq. 7 means $k_p\left\{\frac{2k_t}{k_iK_i}\right\}^{1/2}$, which corresponds to a terms calculated from Eqs. 7, 8, and 11.

TABLE 1. OXIDATION OF CYCLOHEXENE WITH Co(II) TETRA(*p*-TOLYL)PORPHYRIN IN ETHYL ACETATE AT 30 °C

Cyclohexene (M)	CoTPP Complex ($\times 10^3$ M)	O_2 ($\times 10^3$ M)	$-\mathrm{d}[O_2]/\mathrm{d}t$ ($\times 10^7$ M)	$\frac{-\mathrm{d}[O_2]/\mathrm{d}t}{[\mathrm{Cyclohexene}]^{3/2}[\mathrm{CoTPP}]^{1/2}[O_2]^{1/2}}$ ($\times 10^4$ $M^{-3/2}$ s^{-1})
0.5	5.0	2.34[a)]	2.0	1.70
0.8	5.0	2.34[a)]	4.3	1.76
1.0	5.0	2.34[a)]	6.2	1.81
2.0	5.0	2.34[a)]	16.6	1.73
1.0	1.0	2.34[a)]	2.4	1.58
1.0	2.5	2.34[a)]	4.0	1.65
1.0	10	2.34[a)]	8.9	1.84
1.0	5.0	1.54[b)]	4.8	1.74
1.0	5.0	0.92[c)]	3.9	1.60

a) The value at 760 mmHg and at 30 °C. b) The value at 500 mmHg and at 30 °C. c) The value at 300 mmHg and at 30 °C.

TABLE 2. OXIDATION OF 2,5-DIHYDROFURAN WITH Co(II) TETRA(*p*-TOLYL)PORPHYRIN IN ETHYL ACETATE AT 30 °C

2,5-Dihydrofuran (M)	CoTPP Complex ($\times 10^3$ M)	O_2 ($\times 10^3$ M)	$-\mathrm{d}[O_2]/\mathrm{d}t$ ($\times 10^6$ M)	$\frac{-\mathrm{d}[O_2]/\mathrm{d}t}{[\mathrm{2,5\text{-}dihydrofuran}]^{3/2}[\mathrm{CoTPP}]^{1/2}[O_2]^{1/2}}$ ($\times 10^3$ $M^{-3/2}$ s^{-1})
0.5	5.0	2.34	2.7	2.29
1.0	5.0	2.34	8.5	2.48
2.0	5.0	2.34	23.9	2.50
5.0	5.0	2.34	90.8	2.37
1.0	1.0	2.34	3.5	2.31
1.0	2.5	2.34	5.9	2.45
1.0	10	2.34	12.2	2.53
1.0	5.0	1.54	6.3	2.30
1.0	5.0	0.92	5.3	2.22

2,5-dihydrofuran are initiated by molecular oxygen activated on Co(II) tetra(*p*-tolyl)porphyrin (superoxide ion) in a way similar to the autoxidation of acetaldehyde.[6,7)]

$$\mathrm{Co(II)TPP} + O_2 \overset{K_1}{\rightleftharpoons} \mathrm{Co(II)TPP\text{-}O_2}, \tag{9}$$

$$\mathrm{Co(III)TPP\text{-}O_2} + \mathrm{RH} \xrightarrow{k_1} \mathrm{Co(III)TPP\text{-}O_2H} + \mathrm{R}\cdot, \tag{10}$$

$$\text{or } \mathrm{Co(III)TPP\text{-}O_2\dot{R}H}. \tag{11}$$

Table 3 shows the rates of oxygen absorbed for several hydrocarbons (1 M), using Co(II) tetra(*p*-tolyl)porphyrin (5×10^{-3} M) in ethyl acetate at 30 °C. Significant differences in the rates were observable in response to the kind of hydrocarbons. It is, however, a general trend that Co(II) tetra(*p*-tolyl)porphyrin exhibits a higher reactivity toward hydrocarbons which can undergo both oxidation reactions *via* hydrogen abstraction and addition to double bonds.

Among the cyclic compounds with double bonds, monoenes were generally oxidized more easily than dienes, as exemplified by the comparison of cyclohexene with 1,3-cyclohexadiene, and by that of dihydrofuran with furan.

TABLE 3, OXIDATION OF HYDROCARBONS WITH Co(II) TETRA(*p*-TOLYL)PORPHYRIN

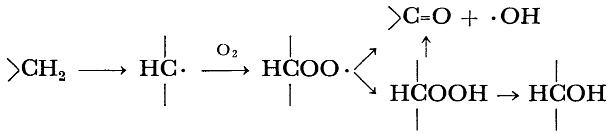
Substrate	$-\frac{\mathrm{d}[O_2]}{\mathrm{d}t}$ [a)], $\times 10^{-7}$ M/s	Modes of oxidation[b)]
Tetralin	0	a
Cumene	0	a
2-Norbornene	≈0	b [c)]
dl-Limonene	≈0	b [c)]
Cyclopentene	6.1	b
Cyclohexene	6.2	b
1-Methylcyclohexene	49	b
4-Methylcyclohexene	8.3	b
1,3-Cyclohexadiene	2.2	b
Cycloheptene	0.9	b
Cyclooctene	49	b
Furan	0.17	c
2,5-Dihydrofuran	85	b [c)]
2,3-Dihydrofuran	9.3	b [c)]

a) [Hydrocarbon]: 1 M, [Co(II) tetra(*p*-tolyl)porphyrin]: 5×10^{-3} M, Solvent: ethyl acetate, 30 °C. b) a: hydrogen abstraction, b: hydrogen abstraction + addition to double bond(s), c: addition to double bond(s). c) Estimated.

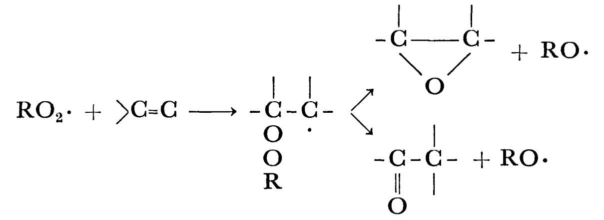
The oxidation products of both cyclohexene and 2,5-dihydrofuran were representatively analyzed. The former substrate gave cyclohexen-2-one (80%), cyclohexan-2-ol (6%), and cyclohexene oxide (13%); this result forms a contrast with the result[10)] obtained by the use of a similar catalyst, Ni(II) phthalocyanine, where 17, 6, and 4% of the above-cited products were obtained respectively. The latter substrate, 2,5-dihydrofuran, on the other hand, formed 2-hydrofuran-5-

one and 2-hydrofuran-5-ol (79%) and 2,3,5-trihydrofuran-4-one (15%).

The products mentioned above, as is well known,[9] are presumably derived from a hydrogen abstraction reaction



and an addition to double bonds



The distribution of these products may suggest the reactivities of the oxygen molecules activated on Co(II) tetra(*p*-tolyl)porphyrin toward hydrocarbons in terms of reaction routes *via* hydrogen abstraction and/or addition to double bonds. This suggestion, however, is apt to be somewhat obscure, because we can observe only overlapped spectra for the distribution of the products which should be derived from peroxyl radicals as well as Co(III)TPP–O_2^-.

*Reactivity of the Oxygen Molecule Activated on Co(II) Tetra(*p*-tolyl)porphyrin.* As shown in Table 3, the modes of the oxidation reactions of hydrocarbons can be classified into those *via* hydrogen abstractions and those *via* additions to double bonds.[11]

The ease of hydrogen abstraction from hydrocarbons is known to be related with the bond dissociation energy between the carbon and hydrogen of the relevant hydrocarbons.[12] Therefore, the hydrogen-abstracting ability of the molecular oxygen, activated on Co(II) tetra(*p*-tolyl)porphyrin, as a free radical can be evaluated by means of the bond-dissociation energy of hydrocarbon, which enters the autoxidation reaction after its initiation by hydrogen abstraction in the presence of the cobalt porphyrin.

The chemical behavior of three types of superoxide ions was compared in terms of the reactivities toward hydrocarbons, which undergo oxidation reactions only *via* hydrogen abstractions. Co(II) tetra(*p*-tolyl)porphyrin and π-allyl $Fe(CO)_3Br$[13] were found to form less reactive superoxide ion than the electrogenerated one. The latter superoxide ion could catalyze, for instance, the autoxidation reactions at 30 °C of 9,10-dihydroanthracene (71 kcal/mol), cumene (79 kcal/mol), tetralin (82 kcal/mol), and cyclohexene (95 kcal/mol), where the numerals in parentheses are the respective C–H bond dissociation energies (D_{C-H}). The former two metal complexes failed to catalyze at 30 °C the autoxidation reaction of cumene and tetralin, which have D_{C-H} values above 79 kcal/mol.

In considering the reactivity of Co(II) tetra(*p*-tolyl)porphyrin toward the cyclic olefins listed in Table 3, it may necessary first to solve the question of which reaction mode, double-bond addition or hydrogen abstraction, is predominant in the autoxidation reaction. In order to determine such a mode of reaction by the molecular oxygen activated on the cobalt–porpyrin catalyst, the rates of initiation for several cyclohexene derivatives were measured.

The rate of initiation, R_i, was determined by measuring the induction period in autoxidation reactions of cyclohexenes with Co(II) tetra(*p*-tolyl)porphyrin in the presence of 2,6-di-*t*-butyl-4-methylphenol at 30 °C. The values for the rate constant were calculated using

$$R_i = k_i K_i [RH][CoTPP][O_2], \tag{12}$$

which can be derived by assuming Reactions 9—11. Table 4 shows the observed values for the rate of initiation, together with the calculated rate constant, $k_i K_i$, of Reaction 12 at 30 °C.

The calculated rate constants of the initiation reactions were found to have a good correlation with the $\nu_{C=C}$ of cyclohexenes as is shown in Fig. 1. It should be noted that the oxygen molecule activated on Co(II) tetra(*p*-tolyl)porphyrin cannot abstract the hydrogen atom from 1-methylcyclohexene, 4-methylcyclohexene, and cyclohexene, because the D_{C-H} values of the cyclic olefins are estimated to be about 82 kcal/mol.[10] 1,3-Cyclohexadiene is also considered to enter the autoxi-

TABLE 4. DETERMINATION OF RATE CONSTANTS (k_i) OF THE INITIATION REACTION IN THE AUTOXIDATION OF CYCLOHEXENE DERIVATIVES WITH Co(II) TETRA(*p*-TOLYL)PORPHYRIN

Substrates	Temp (°C)	$k_p/(2k_t)^{1/2}$ $M^{-1/2}\,s^{-1/2}$	R $M\,s^{-1}$	R_i $M\,s^{-1}$	$k_i K_i$ $M^{-2}\,s^{-1}$
1-Methylcyclohexene	15[a)]	1.56×10^{-3}	4.9×10^{-6}	1.58×10^{-6}	1.4×10^{-1}
	30[b)]	3.90×10^{-3}			
	40[a)]	5.93×10^{-3}			
4-Methylcyclohexene	15[a)]	2.78×10^{-3}	8.3×10^{-7}	4.65×10^{-8}	3.97×10^{-3}
	30[b)]	3.85×10^{-3}			
Cyclohexene	15[a)]	0.6×10^{-3}	6.2×10^{-7}	8.97×10^{-8}	7.67×10^{-3}
	30[b)]	2.07×10^{-3}			
	40[a)]	2.93×10^{-3}			
1,3-Cyclohexadiene	30[a)]	1.0×10^{-9}	2.2×10^{-7}	4.8×10^{-12}	4.14×10^{-5}

a) From Ref. 9. b) This work. Reaction conditions: [cyclohexene derivative]: 1 M, [Co(II) tetra(*p*-tolyl)porphyrin]: 5×10^{-3} M, [O_2]: 2.34×10^{-3} M, in ethyl acetate at 30 °C.

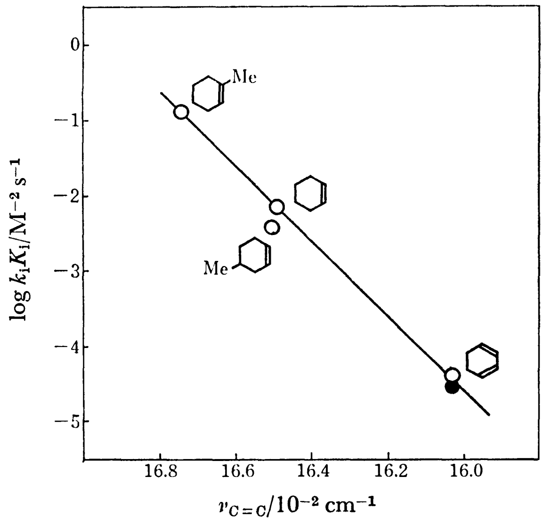


Fig. 1. Correlation of rate constants (k_i) of initiation reaction with $\nu_{C=C}$ of cyclohexene derivatives in autoxidations of the derivatives (1 M) with Co(II) tetra(*p*-tolyl)porphyrin (5×10^{-3} M) under one atom of oxygen at 30 °C.

●: The value calculated by assuming that 73% of 1,3-cyclohexadiene is oxidized through addition reaction.[14)]

dation reaction under the initiation through the addition to the double bond, in light of the previous report[14)] that about 73% of the autoxidation reaction proceeded through the addition reaction, though the D_{C-H} of 1,3-cyclohexadiene is only 71 kcal/mol.[10)]

Therefore, the oxygen molecule activated on Co(II) (*p*-tolyl)porphyrin can be said to react with the double bonds according to an electrophilic addition mechanism, since the value of $\nu_{C=C}$ is regarded as a measure of the electron density of double bonds. From these results and discussion, the reactivity of the activated oxygen molecules can be presumed to be based on the site of the radical.

According to ESR measurement,** the *g*-value of the oxygen molecule activated on Co(II) tetra(*p*-tolyl)porphyrin was 2.012,[6)] which is rather close to that of a peroxy radical (g=2.015),[15)] in contrast with the *g*-value of the electrogenerated superoxide ion (2.006).[6)] These results suggest the following structure for the activated oxygen molecule:[†]

$$\mathrm{Co(II)TPP} + \mathrm{O_2} \rightleftharpoons \mathrm{Co(III)TPP\text{–}^{-}OO\cdot} \qquad (13)$$

The Co(III)TPP–⁻OO· structure can explain the results shown in Fig. 1 in terms of its radical character. The electrophilic reactivity of the oxygen molecule activated on Co(II) tetra(*p*-tolyl)porphyrin should be noticed as a counterpart to the nucleophilic reactivity of other superoxide ions, which are originated, for example, from KO_2.

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** The *g*-values for Co(II)TPP-O_2^- and the electrogenerated superoxide ion were measured at −196 °C in the absence of any substrates to be oxidized.[6)]

[†] The transfer of the spin density from Co(II) to O_2 on complex formation is reported to be about 90% for Co(II)(acacen) and 100% for Co(II)(Schiff base)(base). Such oxygen complexes are formally described as Co(III)-O_2^-. The formal description can be also applied to the cobalt(II) protoporphyrin IX dimethyl ester (see Ref. 16).