Oxidation of Dibenzyl Sulfide *via* an Oxygen Transfer from Palladium Nitrate

Young-ae Whang Park, Yongho Na, and Du-Jong Baek*

*Department of Chemistry, College of Natural Sciences, Sangmyung University, Seoul 110-743, Korea. *E-mail djbaek@smu.ac.kr*

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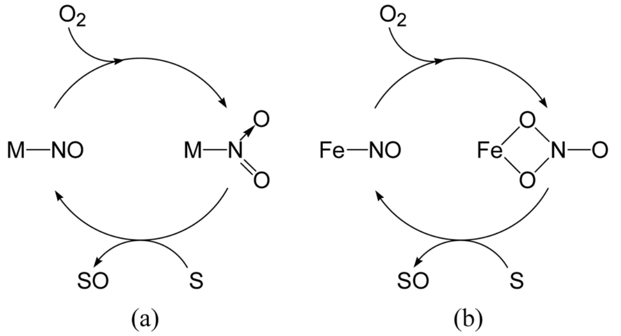
Dibenzyl sulfide was oxidized at the α-carbon to yield benzaldehyde in the presence of $Pd(NO_3)_2$. Oxygen itself could not oxidize the sulfide directly, instead the nitrato ligand of the palladium complex transferred oxygen to dibenzyl sulfide to form benzaldehyde. The X-ray crystal structure of the intermediate complex, *cis*-$[Pd(NO_3)_2\{S(CH_2C_6H_5)_2\}_2]$, revealed that the nitrato ligand was unidentate. Para-substituted dibenzyl sulfides **I**, $(YC_6H_4CH_2)_2S$ wherein Y = OCH_3, CH_3, Cl, CN, or NO_2, were synthesized and reacted with palladium nitrate, and those with electron-donating substituents (Y = OCH_3 and CH_3) were good substrates for the oxidation reaction with palladium nitrate. Thus, the reaction mechanism of the oxygen transfer was proposed to include nucleophilic benzylic carbon.

Key Words : Dibenzyl sulfide, Palladium nitrate, Benzaldehyde, Oxidation

Introduction

Oxidation of organic sulfides by chemical reagents generally yields either sulfoxides or sulfones.[1] On the contrary, radical-induced autoxidation of organic sulfides in the liquid phase proceeds to yield carboxylic acids by the introduction of oxygen into the sulfides at the α-carbon atom.[2] Various organic sulfides are readily autoxidized to acidic products in the base-catalyzed conditions such as potassium *tert*-butoxide-hexamethylphosphoramide system.[3-5] Other non-radical routes for oxidation include the splitting of oxygen molecule on a ligand of a transition metal complex to form a complex with the oxidized ligand, and the oxygen of this ligand would then transfer to organic substrate. This chemistry was first investigated for the nitro/nitrosyl redox couple as shown in Scheme 1(a).[6-8] Transition metal-nitrato complexes are also known to have remarkable reactivity towards organic substrates for several decades.[9,10] Postel and her coworkers demonstrated that iron-nitrato/iron-nitrosyl could also constitute a redox couple (Scheme 1(b)).[11-13] In this redox system, the N-bonded nitrosyl ligand was oxidized by O_2 into a bidentate O-bonded nitrato group which, in turn, transferred oxygen to alkenes or phosphines and was thus reduced to the initial N-bonded nitrosyl group. The nitrate ion has been known to coordinate the metal through oxygen by three different modes as unidentate, bidentate or bridging bidentate.[14,15] Maximum reactivity is observed in the bidentate case as above, thus most of the works on the nitrato/nitrosyl redox couple in the literature deal with bidentate nitrate complexes.



Scheme 1. (a) Nitro/nitrosyl and (b) Nitrato/nitrosyl redox couple. M and S denote transition metal and organic substrate, respectively.

In the case of palladium complex, oxygen transfer reaction *via* palladium-nitrato/palladium-nitrosyl couple has never been reported before, though treatment of $[Pd(NO_3)_2L_2]$ (L=PPh_3 or PEt_3) with NO or CO was reported to cause deoxygenation to give nitro species $[Pd(NO_2)_2L_2]$.[16] Therefore, we report here the first case of the potential unidentate palladium-nitrato/palladium-nitrosyl redox couple for the oxidation of dibenzyl sulfide to benzaldehyde, along with the synthesis and reactions of various para-substituted dibenzyl sulfides for the elucidation of the reaction mechanism of oxygen transfer from palladium nitrate.

Results and Discussion

In our previous work on the dehydrogenation reaction of cyclohexanone with $Pd(NO_3)_2$-dibenzyl sulfide catalytic system, benzaldehyde, the oxidation product of dibenzyl sulfide, was also observed in addition to the dehydrogenated product.[17] In order to verify the oxidant of this reaction dibenzyl sulfide was reacted under O_2, but it did not give benzaldehyde. Then, when dibenzyl sulfide was reacted with $Pd(NO_3)_2$ under O_2, benzaldehyde was observed, and further, the same reaction without O_2 (under N_2) yielded benzaldehyde as well. Therefore, it was proved that the main oxidant in this reaction was $Pd(NO_3)_2$. It is remarkable that benzaldehyde was not oxidized further to benzoic acid even after a long period of time in this reaction condition.

Spectroscopic analysis. The oxidation reaction was monitored with NMR spectroscopy. The mixture of dibenzyl sulfide and $Pd(NO_3)_2$ in benzene-d_6 under O_2 in a sealed NMR tube was gradually heated from ambient temperature to 80 °C in NMR spectrometer. At the beginning, the resonance peak of the benzylic proton of dibenzyl sulfide appeared at 3.3 ppm, and this peak was shifted down to 3.6 ppm as the reaction proceeded, meaning that the sulfide was coordinated to palladium metal. At 50 °C, a new peak at 9.6 ppm started to grow, which indicated that benzaldehyde was beginning to form. At 80 °C, the growth of the peak discontinued after an hour. The reaction was also monitored with IR spectroscopy. When the reaction of dibenzyl sulfide with $Pd(NO_3)_2$ in methylene chloride under N_2 was carried out at 10 °C, orange-red crystalline product, probably the intermediate complex, was isolated. The IR absorption bands of the complex observed at 1480, 1260 and 985 cm^{-1} could be assigned to a unidentate nitrato group. However, as the temperature of the above reaction was raised and brought to reflux, oily product was obtained and a new absorption band appeared at 1688 cm^{-1} in its IR spectrum, indicating the characteristic Pd-NO bond formed by the oxygen transfer from the nitrate. Since Pd-NO complex was isolated only as oil, we could not carry out the reverse reaction to form palladium-nitrato complex from palladium-nitrosyl complex. From the above NMR and IR results, we concluded that dibenzyl sulfide was oxidized to benzaldehyde by transferring oxygen atom from the palladium-nitrato complex and, in turn, the nitrato-ligand itself was reduced to form palladium-nitrosyl complex.

X-ray crystal structure of the intermediate complex. It was proved further that the intermediate complex, the orange-red crystalline product obtained at 10 °C, was *cis*-$[Pd(NO_3)_2\{S(CH_2Ph)_2\}_2]$ by X-ray crystallography as illustrated in Figure 1. Selected bond lengths and bond angles with estimated standard deviations are given in Table 1. The complex is square planar, and the nitrato ligand is bonded through an oxygen atom to the metal as unidentate, which is supported further by the fact that the bond length between nitrogen and the coordinated oxygen (1.32 Å) is longer than those between nitrogen and two uncoordinated oxygen atoms (1.20 Å) by 0.12 Å in the nitrato ligand. It is worth to note that this unidentate nitrato ligand is unique since most of the metal-nitrato complexes undergoing oxygen transfer reaction comprise bidentate nitrato ligands.

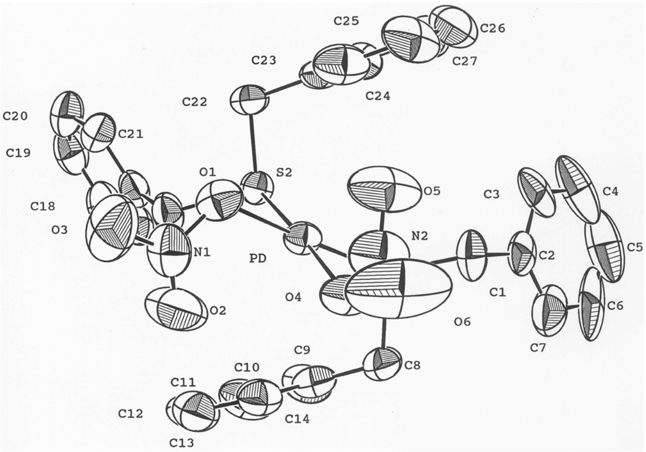


Figure 1. Molecular structure of *cis*-$[Pd(NO_3)_2\{S(CH_2Ph)_2\}_2]$.

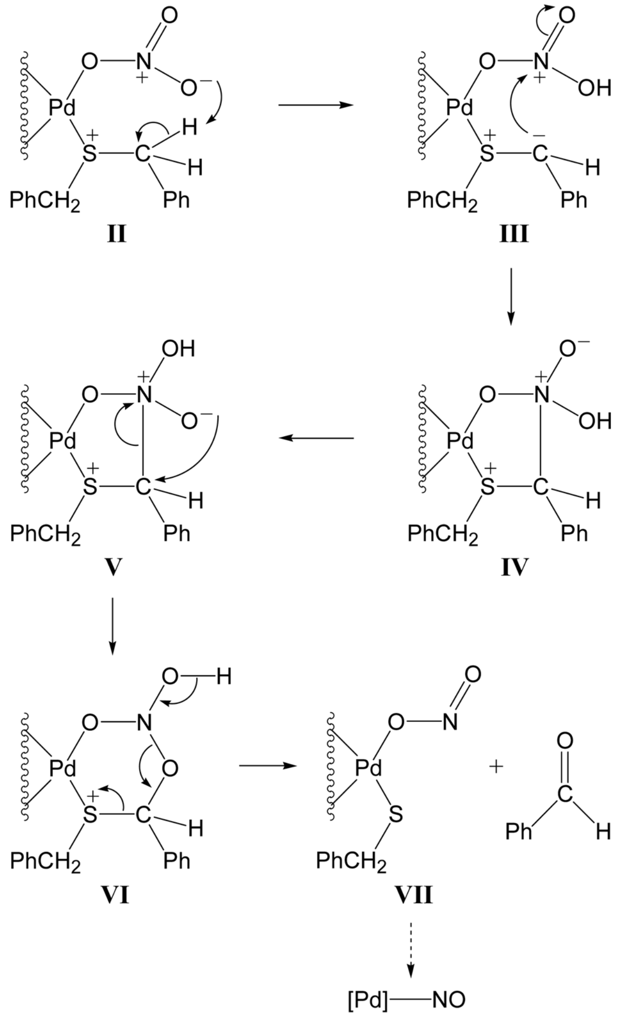
Table 1. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations for *cis*-$[Pd(NO_3)_2\{S(CH_2Ph)_2\}_2]$

$Pd-S_1$	2.258 (2)	N_1-O_1	1.33 (1)
$Pd-S_2$	2.277 (2)	N_1-O_2	1.16 (1)
$Pd-O_1$	2.063 (5)	N_1-O_3	1.22 (1)
$Pd-O_4$	2.053 (7)	N_2-O_4	1.30 (1)
		N_2-O_5	1.23 (1)
		N_2-O_6	1.19 (1)
S_1-Pd-S_2	86.7 (8)	O_1-Pd-O_4	91.6 (2)
S_1-Pd-O_4	91.3 (2)	O_1-Pd-S_2	90.5 (5)
S_1-Pd-O_1	176.8 (2)	S_2-Pd-O_4	175.8 (2)

Synthesis of substituted dibenzyl sulfides and oxidation reactions of the sulfides with palladium nitrate. The *para*-substituted dibenzyl sulfides **I**, $(YC_6H_4CH_2)_2S$ wherein Y = OCH_3, CH_3, Cl, CN, or NO_2, were synthesized from their corresponding benzyl bromides in the presence of sodium sulfide in 40-85% yields. The substituents were chosen as either electron-donating or electron-withdrawing in order to examine whether the mechanism of the oxygen transfer from palladium nitrate was nucleophilic or electrophilic. Each sulfide was reacted with palladium nitrate in toluene by heating to reflux under oxygen, and the generated benzaldehyde was analyzed by GC at various time intervals. The semi-logarithmic plot of the concentration of benzaldehyde against time gave a straight line with a slope of first-order rate constant *k*, and the values for the substituted dibenzyl sulfides are listed in Table 2 along with the yields of the generated benzaldehydes. The rate constant for dibenzyl sulfide **Ic** (Y = H) was 0.072 min^{-1}, and those of **Ie** and **If** (Y = CN and NO_2) were 0.0027 and 0.0030 min^{-1}, respectively. This results show that the reaction rates of the sulfides with strong electron-withdrawing substituents are 24- to 27-fold slower than that of dibenzyl sulfide **Ic**. Contrary to this, the rate constants for sulfides **Ia** and **Ib** with electron-donating substituents (Y = OCH_3 and CH_3) were 0.087 and 0.054 min^{-1}, respectively, similar to that of dibenzyl sulfide **Ic**. Even though the electron-donating substituents in these sulfides **Ia** and **Ib** did not increase the reactivity, however, the maximum amounts of benzaldehydes were 20% and 15%, respectively, which were high enough compared to those of the other reactions (6-9.5%). From these results, it is obvious that the benzylic carbon of dibenzyl sulfide in the $Pd(NO_3)_2$-sulfide complex should be nucleophilic, so we propose the plausible mechanism of formation of benzaldehyde from dibenzyl sulfide in Scheme 2. Initially, oxide ion of the nitrato ligand in structure **II** absorbs a proton at the benzylic carbon producing carbanion, which is quite stabilized by forming ylide with the adjacent sulfonium ion as seen in structure **III**. This benzylic carbanion is nucleophilic, thus attacks the nitronium ion to form 5-membered ring in **IV**. Then, after proton exchange, 6-membered ring is formed as in structure **VI** by the attack of N-oxide in **V** to the benzylic carbon and simultaneous C-N bond cleavage. Finally, base-catalyzed electron transfer and the sequential N-O and C-S bond cleavages result in the generation of benzaldehyde and

Table 2. Oxidation reactions of the para-substituted dibenzyl sulfides with palladium nitrate

$(YC_6H_4CH_2)_2S$	Rate constant (min^{-1})	Yield of YC_6H_4CHO (%)
Ia, Y = *p*-OCH_3	0.087	20
Ib, Y = *p*-CH_3	0.054	15
Ic, Y = H	0.072	6
Id, Y = *p*-Cl	0.066	7.5
Ie, Y = *p*-CN	0.0027	6
If, Y = *p*-NO_2	0.0030	9.5



Scheme 2. Plausible mechanism of the formation of benzaldehyde from dibenzyl sulfide.

palladium-nitro complex **VII**. This nitro complex is further reduced to palladium-nitrosyl complex eventually, and similar mechanisms of the oxygen transfer reactions between metal-nitrato/nitrosyl or metal-nitro/nitrosyl were described in the literature.[18,19]

In conclusion, dibenzyl sulfide was oxidized at the α-carbon to produce benzaldehyde in the presence of $Pd(NO_3)_2$. Oxygen itself could not oxidize the sulfide directly, instead the nitrato ligand of the palladium complex transferred oxygen to dibenzyl sulfide to form benzaldehyde. The X-ray crystal structure of the intermediate complex, *cis*-$[Pd(NO_3)_2\{S(CH_2C_6H_5)_2\}_2]$, revealed that the nitrato ligand was unidentate. Various para-substituted dibenzyl sulfides were synthesized and reacted with palladium nitrate in order to elucidate the reaction mechanism of the oxygen transfer from palladium nitrate. Those with electron-donating substituents (OCH_3 and CH_3) were good substrates for the oxidation reactions, thus the reaction mechanism of the oxygen transfer was proposed to include nucleophilic benzylic carbon.

Experimental Section

General. GC data were collected on a Hewlett Packard 5890 Series II gas chromatograph that employed a FID detector and a HP-5 capillary column (25 m × 0.32 mm), and GC-MS spectra were obtained on a Varian GCMS-3400 spectrometer with a DB-5 column. ^1H NMR spectra were determined at 250 MHz on a Bruker Avance 250 spectrometer, and chemical shifts were reported in δ scale in parts per million from tetramethylsilane as an internal standard. Peak multiplicities were designated as follows: s, singlet; d, doublet; and m, multiplet. IR absorption spectra were taken on a Perkin-Elmer 16F-PC FT-IR spectrometer. Elemental analysis was performed in the Advanced Analysis Center, Korea Institute of Science and Technology. Melting points were determined on a Barnstead/Electrothermal IA9200 apparatus and were uncorrected. Thin-layer chromatography (TLC) was performed with E. Merck silica gel 60 F-254 precoated glass plates (0.25 mm), and flash column chromatography was performed using E. Merck silica gel 60 (40-63 μm).[20] All reagents and solvents were reagent grade, and solvents were purified by published procedures and stored under argon.

Reaction of dibenzyl sulfide under oxygen. A solution of 95 mg of dibenzyl sulfide (0.434 mmol) in 5 mL of methylene chloride in Schlenk flask was flushed with oxygen gas, and the reaction mixture was heated to reflux for 1.5 hr. After cooling, 1 mL of the reaction mixture was added to 2 mL of n-hexane, stirred for 10 min, and filtered through Celite, then the filtrate was analyzed by GC-MS: *m/e* 214 (M^+) for dibenzyl sulfide.

Reaction of dibenzyl sulfide with palladium nitrate. A solution of 95 mg of dibenzyl sulfide (0.434 mmol) and 50 mg of palladium nitrate (0.217 mmol) in 5 mL of methylene chloride in Schlenk flask was flushed with oxygen or nitrogen gas, and the reaction mixture was heated to reflux for 1.5 hr. After cooling, 1 mL of the reaction mixture was added to 2 mL of n-hexane, stirred for 10 min, and filtered through Celite, then the filtrate was analyzed by GC-MS: *m/e* 106 (M^+) for benzaldehyde.

NMR analysis of the reaction of dibenzyl sulfide with palladium nitrate. The ^1H NMR spectrum of a solution of 95 mg of dibenzyl sulfide (0.434 mmol) in 1.5 mL of benzene-d_6 in pressure/vacuum NMR tube was taken at room temperature: δ 3.3 (s, 4H), 7.2-7.4 (m, 10H). Palladium nitrate (50 mg, 0.217 mmol) was added to the NMR tube and the mixture was flushed with oxygen gas, then the valve was closed well, and spectrum was taken: δ 3.6 (s), 7.2-7.4 (m). The temperature was elevated to 50 °C, and after 10 min at this temperature, spectrum was taken: δ 3.6 (s), 7.2-7.4 (m), 9.6 (s). Then, spectra were taken at higher temperatures as follows: after 10 min at 60 °C, after 10 min at 70 °C, and every 15 min for 2 hr at 80 °C.

IR analysis of the intermediate complexes from the reaction of dibenzyl sulfide with palladium nitrate. A solution of 190 mg of dibenzyl sulfide (0.868 mmol) and 100 mg of palladium nitrate (0.434 mmol) in 10 mL of methylene chloride in Schlenk flask was flushed with nitrogen gas maintaining the temperature under 10 °C, and reacted at that temperature for 30 min. Half of the reaction mixture was filtered through Celite, and the orange-red crystals obtained after the evaporation of the solvent were analyzed by IR spectrometer as KBr pellet: 1480, 1260, 985 cm^{-1}. The remaining half of the reaction mixture was heated to reflux for an additional 30 min and filtered through Celite, and the red-brown oil obtained after the evaporation of the solvent was analyzed by IR spectrometer as a neat spectrum: 1688 cm^{-1}.

Determination of the X-ray crystal structure and characterization of the intermediate palladium-nitrato complex. The orange-red crystals obtained under 10 °C as mentioned above were recrystallized with a cold 1 : 1 mixture of methylene chloride and n-hexane to form single crystals suitable for X-ray crystallography analysis: ^{1}H NMR ($CDCl_3$) δ 3.45 (s, 4H), 3.61 (s, 4H), 7.25-7.45 (m, 20H); IR (KBr) 1559, 1494, 1272, 980 cm^{-1}; Anal. Calcd for $C_{28}H_{28}N_2O_6PdS_2$: C, 51.03; H, 4.28; N, 4.25; S, 9.73. Found: C, 51.30; H, 4.29; N, 4.19; S, 9.85. Diffraction data were collected on a Rigaku D/Max-IC X-ray diffractometer at the Center for Scientific Instruments, Kyungpook National University. Crystal data and measurement conditions are shown in Table 3.

Table 3. Crystal data and measurement conditions of *cis*-$[Pd(NO_3)_2\{S(CH_2Ph)_2\}_2]$

Empirical formula	$C_{28}H_{28}N_2O_6PdS_2$
Formula weight	594.94
Crystal system	monoclinic
Space group	$P2_1/n$(#14)
Z	4
Cell parameter	
a (Å)	9.486(3)
b (Å)	32.414(8)
c (Å)	10.067(3)
β (deg)	111.44(2)
Volume (Å^3)	2881(1)
Density (calculated, g/cm^3)	1.519
Absorption coefficient (cm^{-1})	8.2
Transmission factor	90.4212-99.8678
Scan type	ω-2θ
Scan width (ω) (deg)	1.03+1.09tan (θ)
$2\theta_{max}$ (deg)	52.64
No. of reflections measured	6327
No. of reflections observed ($I > 3\sigma(I)$)	3790
F(000)	1216
No. of variables	352
Discrepancy indices	
R	0.0588
R_w	0.0863
Goodness of fit indicator	2.54
Maximum shift in final cycle	less than 0.01

Synthesis of substituted dibenzyl sulfides. To a stirred solution of para-substituted benzyl bromide (20 mmol) in 30 mL of 95% ethanol, was added a solution of 3.36 g (14 mmol) of sodium sulfide nonahydrate in 20 mL of water dropwise. The solution was stirred at room temperature for 40-90 min, then the ethanol was removed by simple distillation. The hot aqueous solution was poured to chipped ice, and after the ice was melted, the solid was filtered, washed with cold water, and dried. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2/n-hexane (1 : 3) to give the properly para-substituted dibenzyl sulfide as follows:

Di(*p*-methoxybenzyl) sulfide (Ia): white solid, 1.29 g (47%): mp 52-54 °C; ^{1}H NMR ($CDCl_3$) δ 3.56 (s, 4H), 3.81 (s, 6H), 6.85 (d, 4H, *J* = 8.7 Hz), 7.20 (d, 4H, *J* = 8.6 Hz); Mass *m/e* 274 (M^+), 153, 121.

Di(*p*-methylbenzyl) sulfide (Ib): white solid, 2.02 g (84%): mp 76.5-78.0 °C; ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 6H), 3.60 (s, 4H), 7.15 (m, 8H); Mass *m/e* 242 (M^+), 137, 105.

Di(*p*-chlorobenzyl) sulfide (Id): white solid, 2.11 g (74%): mp 41-43 °C; ^{1}H NMR ($CDCl_3$) δ 3.56 (s, 4H), 7.16 (m, 8H); Mass *m/e* 282 (M^+), 157, 125.

Di(*p*-cyanobenzyl) sulfide (Ie): white solid, 1.31 g (67%): mp 114.5-115.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.61 (s, 4H), 7.37 (d, 4H, *J* = 7.1 Hz), 7.62 (d, 4H, *J* = 6.9 Hz); Mass *m/e* 264 (M^+).

Di(*p*-nitrobenzyl) sulfide (If): yellow solid, 1.19 g (40%): mp 153.5-156.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.68 (s, 4H), 7.43 (d, 4H, *J* = 8.7 Hz), 8.19 (d, 4H, *J* = 8.8 Hz); Mass *m/e* 304 (M^+), 168, 136.

Measurement of rate constants for the oxidation reactions of substituted dibenzyl sulfides. A solution of a substituted dibenzyl sulfide (0.434 mmol) and palladium nitrate (50 mg, 0.217 mmol) in 5 mL of toluene including 98 mg (0.434 mmol) of hexadecane as an internal standard was heated to reflux with oxygen gas bubbling slowly through a syringe needle. The amounts of the substituted benzaldehyde generated in the reaction were determined at various time intervals by transferring 0.1 mL of aliquot into 0.2 mL of n-hexane in dry ice bath. After the mixture was filtered through Celite, the filtrate was analyzed by GC-MS. The semilogarithmic plot of the amounts of the benzaldehyde against time gave a straight line with a slope of first-order rate constant *k*.

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