

^1H and ^{17}O NMR spectroscopic detection and characterization of titanium(IV) alkylperoxo complex

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Abstract

Using ^1H and ^{17}O NMR spectroscopy it was shown that in the initial stage of the reaction of $\text{TiO}(\text{acac})_2$ (Hacac = acetylacetone) with an excess of Me_3COOH in benzene an alkylperoxo complex $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$ is formed. The mode of generation of this alkylperoxo complex (via addition of Me_3COOH to $\text{Ti}=\text{O}$ bond) differs from that previously observed for alkylperoxo complexes of vanadium(IV) and molybdenum(VI) (via oxidative addition or ligand substitution, respectively). $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$ is probably octahedral with acetylacetonato ligands occupying equatorial positions.

Keywords: Alkylperoxo complexes; Titanium; Epoxidation; Mechanisms

1. Introduction

It is widely agreed that transition metal alkylperoxo complexes MOOR (where $\text{M}=\text{Mo}$, V , Ti) are active species in the selective epoxidation of alkenes with organic hydroperoxides [1–5]. However, in the case of titanium(IV) very little information is available about the reaction mechanism. Titanium(IV) alkylperoxo complexes have never been synthesized or detected spectroscopically. At the same time $\text{Ti}(\text{IV}) + \text{ROOH}$ catalytic systems are of great practical importance. To mention just two of them: $\text{Ti}(\text{IV})$ supported on SiO_2 is a unique catalyst in selective epoxidation of propylene by organic hydroperoxides [1], and the catalytic system titanium(IV) tetraisopropoxide, tert-butyl hydroperoxide, and (+) or

(–)-diethyl tartrate has shown its potential for the asymmetric epoxidation of allylic alcohols [2].

Recently, the reaction of $\text{Ti}(\text{OtBu})_4$ with enriched in ^{17}O cumene hydroperoxide was investigated with ^{17}O NMR spectroscopy [3]. Addition of 1 equiv. of the hydroperoxide to $\text{Ti}(\text{OtBu})_4$ shows little free hydroperoxide (resonances at 258 (800 Hz) and 216 ppm (600 Hz)) in solution and a single peak at 284 ppm (1 kHz) assigned to the alkylperoxide product $[\text{Ti}(\text{OtBu})_3(\text{OOCMe}_2\text{Ph})]_n$ [3]. However, further studies are needed to support this assignment. It is unclear, why the resonance at 284 ppm is of practically the same width as those of free cumene hydroperoxide. The widths of the resonances of quadrupole nuclei dramatically increases with the growth of the size of molecule [4]. From the experimental data available it is difficult to

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exclude that the resonance at 284 ppm belongs to OtBu groups but not to the OOCMe_2Ph moiety (natural abundance $\text{Ti}(\text{OtBu})_4$ exhibits resonance at 303 ppm (300 Hz) [3]).

In our previous works we have observed and characterized spectroscopically alkylperoxo complexes formed in reactions of $\text{VO}(\text{acac})_2$ and $\text{MoO}_2(\text{acac})_2$ with Me_3COOH in benzene [6,7]. In this work we have detected with ^1H and ^{17}O NMR the titanium(IV) alkylperoxo complex formed in the initial step of reaction of $\text{TiO}(\text{acac})_2$ with Me_3COOH .

It was interesting to compare the mode of generation of titanium(IV) alkylperoxo complexes and that of vanadium(V) and molybdenum(VI). Note that the catalytic system $\text{TiO}(\text{acac})_2 + \text{Me}_3\text{COOH}$ can epoxidize cyclohexene [8].

2. Experimental

Benzene- d_6 was dried over sodium metal. $\text{TiO}(\text{acac})_2$ and tert-butyl hydroperoxide were synthesized as described in ref. [9] and [10,11], respectively. Purchased cyclohexene was purified by double fractional distillation just before using. Reactions were carried out directly in standard NMR tubes at 293 K by addition of Me_3COOH to solutions of $\text{TiO}(\text{acac})_2$.

^1H and ^{17}O NMR spectra were recorded at 400.13 and 54.043 MHz, respectively, using the pulsed FT NMR technique on a Bruker MSL 400 MHz spectrometer. The field homogeneity was adjusted by shimming on the ^2H resonance of deuterated solvents. A high-power probe head was used for ^{17}O NMR measurements to increase sensitivity.

The following operating conditions were used for ^{17}O NMR measurements: sweep width 80 000 Hz, spectrum accumulation frequency 100 Hz, number of scans 30 000–200 000, 90° radio frequency pulse at 13 μs . The data were accumulated with 2K data points in the time domain and were transformed with optimal exponential multiplication 20–50 Hz. Chemical shifts were calculated

in ppm with positive values in the low-field direction with respect to the reference: TMS for ^1H and H_2O for ^{17}O . The error in measuring the ^{17}O chemical shift values was ± 1 ppm for the line widths below 500 Hz, and that for measuring a line width was ± 20 Hz for the line widths between 100 and 400 Hz.

The EPR spectra were recorded using a Bruker ER 200 D spectrometer. The concentration of $\text{Me}_3\text{COO}^\cdot$ free radicals was measured by comparing the second integrals of the EPR spectra of the sample and a 0.1 mg crystal of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ as reference.

3. Results and discussion

3.1. The structure of $\text{TiO}(\text{acac})_2$ in benzene and chloroform

According to molecular weight determination, $\text{TiO}(\text{acac})_2$ exists in benzene mainly in the form of dimers $[\text{TiO}(\text{acac})_2]_2$ [9].

The ^1H NMR spectrum of a 0.20 M solution of $\text{TiO}(\text{acac})_2$ in C_6D_6 includes at least two types of titanium(IV) complexes (Fig. 1a). Two narrow signals with relative intensities 1:6, denoted by

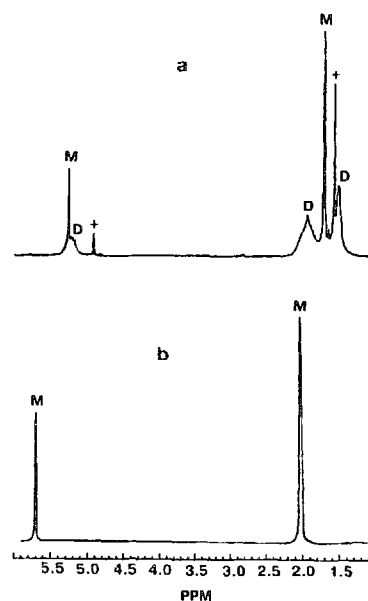
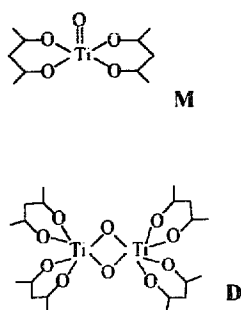


Fig. 1. ^1H NMR spectrum of 0.20 M $\text{TiO}(\text{acac})_2$: (a) in C_6D_6 ; (b) in CDCl_3 . The lines marked by crosses correspond to free acetylacetonate (enol).

the letter M, most probably belong to acetylacetonato ligands of monomeric complex $\text{TiO}(\text{acac})_2$, three broad lines with relative intensities 1:3:3 (D) are assigned to that of the dimeric complex $[\text{TiO}(\text{acac})_2]_2$. The lines marked by crosses correspond to free acetylacetonone (enol) (see Fig. 1a and Table 1).



In agreement with molecular weight determination, $[\text{TiO}(\text{acac})_2]_2$ prevails in C_6D_6 . The ratio [dimer]/[monomer] calculated from the spectrum of Fig. 1a is 4. Nonequivalence of CH_3 groups of acetylacetonato ligands of complex D (Fig. 1a) supports its attribution to $[\text{TiO}(\text{acac})_2]_2$.

The ^{17}O NMR spectrum of the same sample is presented in Fig. 2a. The broad line at 350 ppm was assigned to the oxygen atoms of acetylacetonato ligands of $[\text{TiO}(\text{acac})_2]_2$. The correspond-

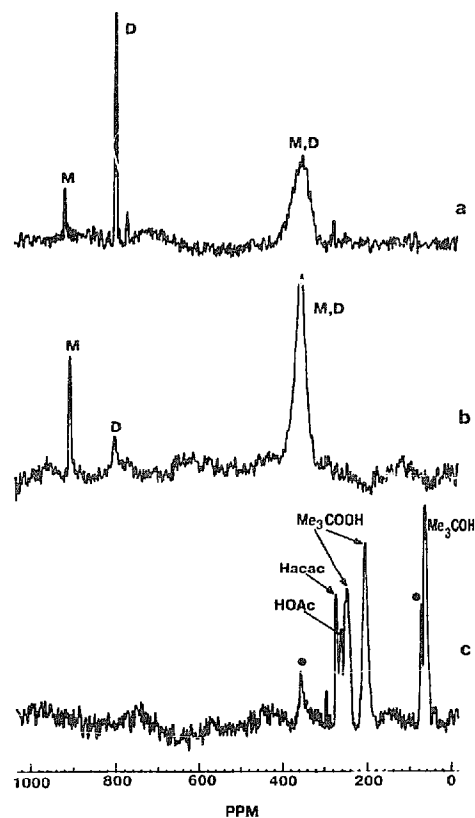


Fig. 2. ^{17}O NMR spectrum of 0.20 M $\text{TiO}(\text{acac})_2$: (a) in C_6D_6 ; (b) in CDCl_3 ; (c) 15 min after onset of reaction of $\text{TiO}(\text{acac})_2$ with Me_3COOH in C_6D_6 ($[\text{Me}_3\text{COOH}] = 3.0 \text{ M}$). Number of scans = 100 000.

ing line of the monomer $\text{TiO}(\text{acac})_2$ is masked by this line. The line at 796 ppm (marked by D) was attributed to Ti-O-Ti oxygen atoms of

Table 1
 ^{17}O and ^1H NMR chemical shifts δ and line widths $\Delta\nu_{1/2}$ of titanium(IV) complexes in C_6D_6 and CDCl_3

Complex	Solvent	δ/ppm ($\Delta\nu_{1/2}/\text{Hz}$)						
		^{17}O			^1H			
		Ti-O-Ti	Ti=O	acac	CH^{acac}	$\text{CH}_3^{\text{acac}}$	$\text{CH}_3^{\text{OOCMe}_3}$	$\text{CH}_3^{\text{OCMe}_3}$
$\text{TiO}(\text{acac})_2$	C_6D_6	–	917 (200)	–	5.28	1.73	–	–
	CDCl_3	–	903 (360)	346 (1560)	5.64	2.01	–	–
$[\text{TiO}(\text{acac})_2]_2$	C_6D_6	796 (280)	–	350 (2300)	5.22	1.96 1.53	–	–
$\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$	C_6D_6	–	–	360 (1000)	5.30	1.67	1.29	–
	CDCl_3	–	–	–	5.87	2.11	–	–
$\text{Ti}(\text{acac})_2(\text{OCMe}_3)_2$	C_6D_6	–	–	388 ^a (730)	5.26	1.78	–	1.54
		–	–	358 ^a (730)	–	1.86	–	–
		–	–	325 ^a (810)	–	–	–	–

^a It is difficult to distinguish the resonances of acac ligands from those of OCMe_3 ligands.

$[\text{TiO}(\text{acac})_2]_2$ and the line at 917 ppm (marked by M) to Ti=O group of $\text{TiO}(\text{acac})_2$ (see Fig. 2a and Table 1).

The ratio [dimer]/[monomer] dramatically changes when C_6D_6 is replaced by CDCl_3 . Narrow resonances of the monomeric complex $\text{TiO}(\text{acac})_2$ prevail in ^1H (Fig. 1b) and ^{17}O (Fig. 2b) spectra of the 0.2 M $\text{TiO}(\text{acac})_2$ solution in CDCl_3 .

Thus, $\text{TiO}(\text{acac})_2$ exists in C_6D_6 mainly as the dimer $[\text{TiO}(\text{acac})_2]_2$, whereas in CDCl_3 it is present as the monomer $\text{TiO}(\text{acac})_2$.

3.2. Characterization of titanium(IV) alkylperoxo complex $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$

It would be natural to study the reaction of $\text{TiO}(\text{acac})_2$ with Me_3COOH in CDCl_3 , since more simple monomeric species predominate in this solvent. However, in CDCl_3 the ^1H NMR signal of the Me_3COO group of $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$ is masked by the intense signal of Me_3COOH . Hence the experiments were mainly made in C_6D_6 with a 15-fold excess of Me_3COOH to $\text{TiO}(\text{acac})_2$. In this case the ^1H NMR spectrum of alkylperoxo complex was clearly observed.

The ^1H NMR spectra recorded at various lengths of time after onset of the reaction between $\text{TiO}(\text{acac})_2$ and Me_3COOH in C_6D_6 show that at the initial stage resonances with relative intensities 2:12:9 (marked by points) appear and then gradually diminish (Fig. 3 and Table 1). Resonances 2:12 are in the region typical for CH and CH_3 -protons of acetylacetonato ligands. The chemical shift of the resonance with relative intensity 9 (1.29 ppm) is very close to that observed for Me_3COO group of $\text{VO}(\text{acac})_2(\text{OOCMe}_3)$ (1.28 ppm) [6]. It is natural to suppose that the characteristic pattern 2:12:9 belongs to a titanium(IV) complex with a formal monomeric $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$ or dimeric $[\text{Ti}(\text{acac})_2(\text{OOCMe}_3)]_2\text{O}$ structure. For the other possible structures, e.g. $\text{TiO}(\text{acac})(\text{OOCMe}_3)$ and

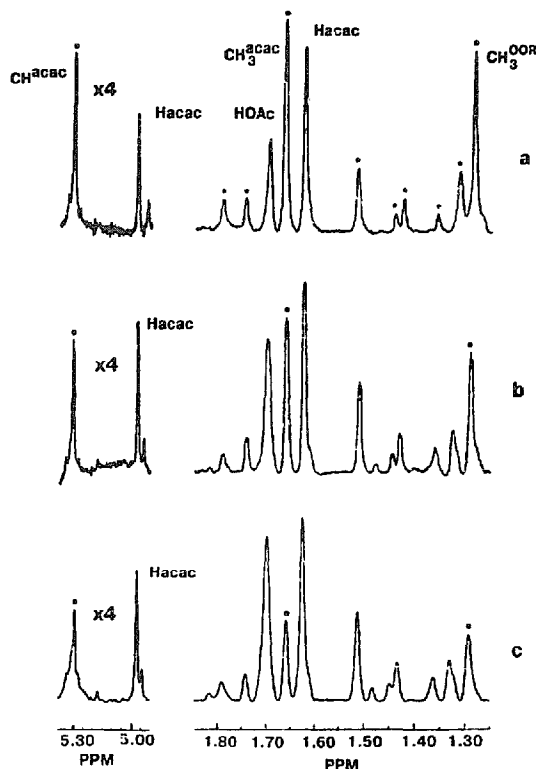


Fig. 3. ^1H NMR spectrum of 0.20 M $\text{TiO}(\text{acac})_2$ in C_6D_6 after various lengths of time after onset of reaction with Me_3COOH ($[\text{Me}_3\text{COOH}] = 3.0 \text{ M}$): (a) 5 min, (b) 15 min, (c) 30 min. Lines marked by asterisks were not reliably identified.

$\text{Ti}(\text{acac})_2(\text{OOCMe}_3)_2$, the ratio of integral intensities of the lines would be 1:6:9.

In the course of the reaction studied, Me_3COOH decomposes to give Me_3COH , whereas acetylacetonate oxidizes into acetic acid.

The lines marked in the Fig. 3a by asterisks were not reliably identified. The first three lines from the left closely resemble those for $\text{Ti}(\text{acac})_2(\text{OCMe}_3)_2$ (see below), the other ones most probably belong to the unidentified products of the oxidation of the acetylacetonate ligands.

On passing from C_6D_6 to CDCl_3 as a solvent, the picture was practically the same as in Fig. 3, but the line of the Me_3COO group of $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$ was masked by the intense signal of Me_3COOH .

^{17}O NMR data provide evidence in favor of the absence of Ti=O or Ti–O–Ti groups in the alkylperoxo complex found. The ^{17}O NMR spectrum of the same sample as in Fig. 3b contains no signals in the region typical for Ti–O–Ti or Ti=O oxygen atoms (see Fig. 2c). Thus, the monomeric

structure $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$ fits the experimental data better than the dimeric one $[\text{Ti}(\text{acac})_2\text{OOCMe}_3]_2\text{O}$. The line near 360 ppm (Fig. 2c) is ascribed to oxygen atoms of acetylacetonato ligands of $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$. The nature of the signal at 73 ppm is still unclear.

The characteristic pattern 2:12:9 in the ^1H NMR spectrum belongs to $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$, but not to $\text{Ti}(\text{acac})_2(\text{OCMe}_3)\text{OH}$. This deduction is based, firstly, on the fact that $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$ decomposes with time in C_6D_6 . The rate of this decomposition increases (ca. twofold), if cyclohexene had been previously added to C_6D_6 ($[\text{C}_6\text{D}_{10}] = 2 \text{ M}$). The decomposition of $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$ in $\text{C}_6\text{D}_6/\text{C}_6\text{H}_{10}$ mixture was accompanied by the growth of the resonances of cyclohexene oxide in the ^1H NMR spectra. Thus, the titanium(IV) complex found, reacts with cyclohexene. Secondly, $\text{Me}_3\text{COO}^\cdot$ free radicals ($[\text{Me}_3\text{COO}^\cdot] \approx 10^{-5} \text{ M}$) were observed in the reaction solution studied. Their concentration changed in a correlated manner with the concentration of $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$. Such an effect was previously observed for alkylperoxo complexes of V, Mo and Co [6,7,12]. Thirdly, we have prepared the complex $\text{Ti}(\text{acac})_2(\text{OCMe}_3)_2$ in situ by heating $\text{TiO}(\text{acac})_2$ for 10 min at 80°C in a $\text{C}_6\text{D}_6/\text{Me}_3\text{COH} = 1:1$ mixture ($[\text{TiO}(\text{acac})_2] = 0.20 \text{ M}$). $\text{Ti}(\text{acac})_2(\text{OCMe}_3)_2$ exhibits in the ^1H NMR spectrum four lines with relative intensities 1:3:3:9 of two acetylacetonato ligands (1:3:3) and two Me_3CO groups (9) (Fig. 4a and Table 1). The ^{17}O NMR spectrum of $\text{Ti}(\text{acac})_2(\text{OCMe}_3)_2$ contains three lines of equal intensity, which belong to nonequivalent oxygen atoms of acetylacetonato ligands and of Me_3CO groups (Fig. 4b and Table 1). The ^1H chemical shift of the Me_3CO group of $\text{Ti}(\text{acac})_2(\text{OCMe}_3)_2$ (1.55 ppm) differs noticeably from that of the Me_3COO group of $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$ (1.28 ppm).

Thus, in the initial stage of the reaction of Me_3COOH with $\text{TiO}(\text{acac})_2$ in benzene an alkylperoxo complex $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$, active towards cyclohexene, is formed.

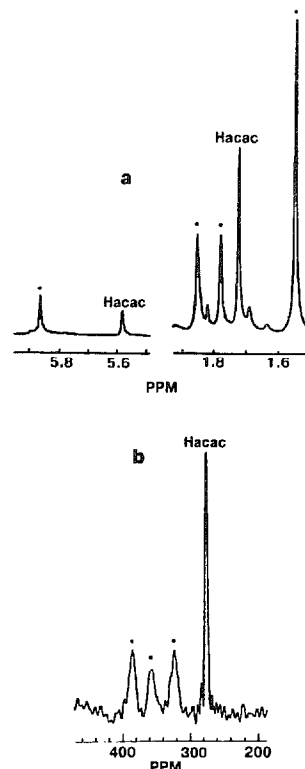
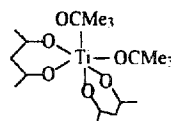
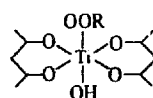


Fig. 4. ^1H (A) and ^{17}O (B) NMR spectra of 0.2 M $\text{Ti}(\text{acac})_2(\text{OCMe}_3)_2$ obtained upon heating of $\text{TiO}(\text{acac})_2$ at 80°C for 10 min in $\text{C}_6\text{D}_6/\text{Me}_3\text{COH} = 1:1$ volume mixture. Spectra were recorded at 20°C . The lines of $\text{Ti}(\text{acac})_2(\text{OCMe}_3)_2$ are marked by points.

Let us consider the possible structure of $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$ in C_6D_6 . According to the ^1H NMR data, the CH_3 groups of its acetylacetonato ligands are equivalent, in contrast to $\text{Ti}(\text{acac})_2(\text{OCMe}_3)_2$. Such equivalence may arise if acetylacetonato ligands occupy the equatorial positions of the octahedral complex. The proposed structures of $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$ and $\text{Ti}(\text{acac})_2(\text{OCMe}_3)_2$ in benzene are presented below.



The mode of generation of $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$ differs from those pre-

viously reported for vanadium(V) and molybdenum(VI) alkylperoxo complexes. $\text{VO}(\text{acac})_2$ reacts with Me_3COOH to give $\text{VO}(\text{acac})_2(\text{OOCMe}_3)$ via oxidative addition [5]. $\text{MoO}_2(\text{acac})_2$ gives $\text{MoO}_2(\text{OOCMe}_3)_2$ via ligand substitution [7]. $\text{TiO}(\text{acac})_2$ interacts with Me_3COOH via addition to the $\text{Ti}=\text{O}$ or $\text{Ti}-\text{O}-\text{Ti}$ bond.

The formation of the titanium(IV) alkylperoxo complex via addition to the $\text{Ti}=\text{O}$ bond was recently proposed, but has not been spectroscopically confirmed [1]. Note that the suggested structure of the active site of the above mentioned Ti(IV)/ SiO_2 supported catalyst includes a $\text{Ti}=\text{O}$ group [1].

It is obvious that $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$ is not the key intermediate of selective epoxidation of cyclohexene by the catalytic system $\text{TiO}(\text{acac})_2 + \text{Me}_3\text{COOH}$, since it exists only at the early stage of the reaction and then irreversibly decomposes (acetylacetonato ligands oxidize into acetic acid). We still have not identified the titanium(IV) alkylperoxo species which drive the catalytic cycle of cyclohexene epoxidation. This was done earlier for vanadium [6] and molybdenum [1,7] complexes as catalysts. However, by analogy we can suppose that titanium(IV) complexes containing 1,2-diol ligands and a Me_3COO group are the active species of cyclohexene epoxidation in the steady-state conditions.

4. Conclusions

An alkylperoxo complex $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$, active towards cyclohexene, is

formed in the initial stage of the reaction of $\text{TiO}(\text{acac})_2$ with Me_3COOH . The mode of generation of $\text{Ti}(\text{acac})_2(\text{OOCMe}_3)\text{OH}$ (via addition to $\text{Ti}=\text{O}$ bond) differs from that of vanadium and molybdenum alkylperoxo complex recently studied. The alkylperoxo complex observed is probably octahedral in structure with acetylacetonato ligands occupying equatorial positions.

Acknowledgements

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