BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1204—1208 (1973)

The Catalytic Effect of the Bismuth Nitrate on the Autoxidation of Olefins

Fujio Tsuchiya and Tsuneo Ikawa
Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo

(Received March 9, 1972)

The catalytic effect of the bismuth nitrate on the autoxidation of olefins has been investigated. Nitrogen dioxide, oxygen atoms, and bismuth oxynitrate, which are the thermal decomposition products of the bismuth nitrate, are not involved in the initiation of the reaction. The bismuth nitrate is only effective on olefinic compounds, not on saturated hydrocarbons, and it does not decompose hydroperoxide. The catalysis of the bismuth nitrate is supposed to result from direct interaction with olefin.

Metal-ion catalysts have generally been used in autoxidation in the form of metal salts of organic acids, and the catalyses of metal ions on the autoxidation of hydrocarbons are classified into the following three effects on the initial step of the oxidation: the formation of alkoxy and alkylperoxy radicals by the metal-ion-catalyzed decomposition of hydroperoxide, the formation of alkyl radicals from hydrocarbons by a higher valent metal ion, and the formation of radicals by the metal-oxygen complex.[1)]

In the previous paper,[2)] it has been reported that the bismuth nitrate is the most effective catalyst among many bismuth compounds as an initiator for the oxidation of isobutene. In this paper, the mechanism of catalysis by the bismuth nitrate has been mainly investigated from the point of view of the character of the nitrate. The effect of nitrogen dioxide, oxygen atoms, and bismuth oxynitrate, which may be formed from bismuth nitrate by its thermal decomposition during the reaction, have been examined, but their formation and contribution have been negligibly small. Iodometric observation has been undertaken in order to ascertain whether or not the bismuth nitrate decomposes hydroperoxide to active free radicals; it has been found not to decompose hydroperoxide. The autoxidation of nonolefinic hydrocarbons, such as cumene and tetralin, has not been catalyzed by the bismuth nitrate. The catalysis of the bismuth nitrate can not be attributed to the three mechanisms mentioned above, but can be assumed to result from the direct interaction between the bismuth nitrate and the double bond of olefin.

Experimental

A stainless autoclave with a reservoir and a magnetic stirrer[2)] was used for the autoxidation of olefins. The volume of the reaction mixture was kept at 50 ml; the total pressure, 20 kg/cm^2; the partial pressure of oxygen, 5 kg/cm^2, and the reaction temperature, 100°C. Acetonitrile was used as the solvent. The oxidation of cyclohexene and some saturated hydrocarbons has been carried out in an oxygen-absorption apparatus[3)] under atmospheric pressure. Iodometry was carried out by means of the chloroform method.[4)]

The gaseous olefins were 99.0% pure grade. Cyclohexene and other hydrocarbons were purified by distillation in a nitrogen atmosphere. The glycerol was of a chemical pure grade. The metal nitrates, stored in a dark ice box, were of a chemical pure grade and were used without further purification. The nitrogen dioxide was obtained by the thermal decomposition of the lead nitrate at 500°C and was stored in a dry ice box.

Gas chromatography was used to analyse the reacted and unreacted substances; the volatile substances using a 3-m column of polyethylene glycol(PEG) 1000 at 80°C; the nonvolatile substances using temperature-programed gas chromatography with a 3-m column of PEG 20M, and unreacted butenes using a 5-m column of benzyl cyanide-$AgNO_3$ at room temperature.

Results and Discussion

Decomposition of Hydroperoxide. The bismuth nitrate oxidized potassium iodide to iodine, and the

Table 1. Iodometry[4)] of bismuth nitrate and cumyl hydroperoxide at 50°C

$Bi(NO_3)_3$ (mol)	CHPO[a)] (mol)	I_2[b)] (mol)	$I_2/Bi(NO_3)_3$[c)]
6.5×10^{-6}		9.0×10^{-6}	1.3
75.9		70.5	0.9
7.6	21.4×10^{-6}	33.9	1.2[d)]
77.8	42.9	115.7	1.0[d)]

a) Cumyl hydroperoxide. b) Isolated iodine. c) Molar ratio of isolated iodine to $Bi(NO_3)_3$. d) Molar ratio of isolated iodine to $(Bi(NO_3)_3+CHPO)$.

---

1) Y. Kamiya, *Yuki Gosei Kagaku Kyokai Shi*, **26**, 957 (1968).

2) F. Tsuchiya, T. Sumi and T. Ikawa, *Kogyo Kagaku Zasshi*, **74**, 2074 (1971).

3) T. Ikawa, M. Muto and T. Shintani, *Bull. Jap. Petrol. Inst.*, **7**, 42 (1965).

4) Y. Ogata, "Chemistry of Organic Peroxide," p. 91, Nankodo, Tokyo (1971).

5) W. F. Brill and B. J. Barone, *J. Org. Chem.*, **29**, 140 (1964).

amount of iodine produced was measured by iodometry in a chloroform solution. The results are tabulated in Table 1. The iodine isolated increased with the increase in the amount of the bismuth nitrate, but the molar ratio of the iodine isolated to the initially-added bismuth nitrate was nearly constant. Then, the bismuth nitrate was added into an acetonitrile solution of cumyl hydroperoxide and iodemetry was carried out on this mixture. The amount of iodine thus isolated was equal to the sum of the quantities of iodine which were obtained in each iodometry of the bismuth nitrate and cumyl hydroperoxide (Table 1). These were increased in the amounts of the bismuth nitrate and cumyl hydroperoxide initially added, but the total amount of iodine was nearly equal to the sum of the individual quantities of iodine (Table 1). From these results, we consider that the bismuth nitrate does not decompose hydroperoxide in the atmosphere.

The Autoxidation of Nonolefinic Hydrocarbons in the Presence of the Bismuth Nitrate. The autoxidation of nonolefinic hydrocarbons, such as tetralin, cumene, and *p*-xylene, was carried out in the presence of the bismuth nitrate; the results are listed in Table 2. The induction periods were very long, even in the presence of the bismuth nitrate, on the autoxidation of saturated hydrocarbons. Although cumene has an active tertiary hydrogen atom, on which can easily be abstracted, no oxygen absorption was observed. This indicates that the bismuth nitrate promotes only the autoxidation of olefins and that the catalytic effect is not based on the direct hydrogen abstraction from an organic compound by a metal ion, such as a higher valence metal ion or a metal-oxygen complex.

TABLE 2. AUTOXIDATION OF NONOLEFINIC HYDROCARBONS IN THE PRESENCE OF BISMUTH NITRATE; INDUCTION PERIOD

Hydrocarbons	Temp (°C)[a]	Induction period (min)	
Tetralin	70	125	A[b]
Cumene	70	154	A
p-Xylene	100	420	P[c]
Cyclohexanone	100	310	P
α-Methylstyrene	60	2	A
Cyclohexene	60	4	A
2-Hexene	60	4	A

a) Reaction temperature. b) Pressure: 1 atom of O_2.
c) Total pressure: 20 kg/cm^2, partial pressure of O_2; 5 kg/cm^2, Hydrocarbon: 4.9 mol/l, solvent: acetonitrile, Bismuth nitrate: 6.2×10^{-4} mol.

The Effect of Metal Nitrates. Metal nitrates such as cobaltous, manganous, ferric, and lead nitrates, were added to a solution of isobutene in order to investigate the effect of nitrates. The results are shown in Table 3. The nitrate effect was observed in the cases of ferric nitrate and the bismuth nitrate; some oxygen was absorbed, and some products, such as acetone and isobutene oxide, were obtained. The cobaltous and manganous nitrates scarcely promoted the oxidation, while these metal salts of organic acids are known to be effective catalysts for the autoxidation of hydrocarbons. This is interesting phenomenon and must be due to the ligand effect of a metal complex. The lead nitrate did not have promoting effect at all.

These nitrates oxidized potassium iodide to iodine; the results are tabulated in Table 4. The amounts of iodine isolated per mole of each metal nitrate were nearly equal to one another except for the ferric nitrate. For the ferric nitrate, the higher value of iodine may be due to the higher valence of the ferric ion. However, this oxidizing ability does not correspond to the promoting effect of the autoxidation.

The decomposition temperatures of the metal nitrates, which were taken from the literature, are also tabulated in Table 4. The promoting effect of the nitrate corresponded to the decomposition temperature of the nitrate except for the cobaltous nitrate; the bismuth nitrate and the ferric nitrate, which decompose at comparatively low temperatures, were effective promoters, and the lead nitrate, which decomposes at a very high temperature, did not have any promoting effect at all. From these results, it can be supposed that nitrogen dioxide, the oxygen atom, and bismuth oxynitrate, which may be formed by the thermal decomposition of the bismuth nitrate during the oxidation of hydrocarbons in the presence of the bismuth nitrate, will contribute to the initial step of the oxidation. Therefore, it became necessary to examine whether or not, nitrogen dioxide, the oxygen atom, and bismuth oxynitrate participate in the initiation of the reaction.

First of all, the effect of nitrogen dioxide was exa-

TABLE 3. THE EFFECT OF METAL NITRATE ON THE AUTOXIDATION OF ISOBUTENE

Metal nitrate	Conversion of *iso*-C_4H_8	Absorbed O_2	Products (Selectivity[a] mol%)					
			CH_3COCH_3	*iso*-BO[b]	*tert*-BuOH[c]	PO[d]	A[e]	E[f]
$Mn(NO_3)_2$	9.1%	3.0 mmol	5.9	—[g]	19.0	2.6	15.7	58.2
$Fe(NO_3)_3$	24.1	24.8	26.4	—	26.3	3.2	8.4	30.6
$Pb(NO_3)_2$	—	—	0	0	0	—	—	—
$Co(NO_3)_2$	5.0	6.4	8.4	—	—	—	0.4	52.3
$Bi(NO_3)_3$[h]	34.2	35.2	23.1	2.5	12.3	0.4	8.9	7.5

iso-C_4H_8: 3.4 mol/l, Metal nitrate: 0.01 mol, solvent: CH_3CN 100 ml, total pressure: 20 kg/cm^2, partial pressure of O_2: 5 kg/cm^2, reaction time; 160 min, reaction temp 100°C.
a) Calculated from the reacted butene. b) Isobutene oxide. c) *tert*-Butyl alcohol. d) Peroxide. e) Acid. f) Ester.
g) Trace-amount. h) *iso*-Butandiol was produced (33.0 mol%).

Table 4. Iodometry and decomposition temperature of nitrates

Nitrates	I_2[a)]	Decomposition temp (°C)[b)]
$Mn(NO_3)_26H_2O$	2.3	129.4
$Fe(NO_3)_39H_2O$	9.8	47.2
$Pb(NO_3)_2$	1.5	470
$Co(NO_3)_26H_2O$	4.8	50
$Bi(NO_3)_35H_2O$	1.20	30

a) The molar ratio of I_2 isolated from KI by nitrate to the nitrate initially added, at 100°C. b) The value taken from those in Ref. 13.

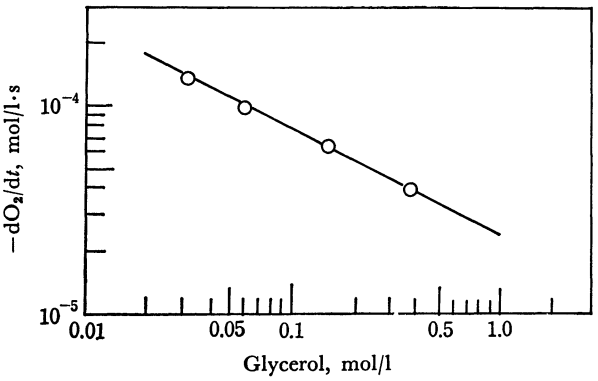

Fig. 1. Glycerol effect on the oxidation of C_6H_{10}.
C_6H_{10}; 4.9 mol/l, 70°C, $Bi(NO_3)_35H_2O$; 2.2×10^{-4} mol solvent; acetonitrile, reaction mixture; 10 ml

mined; a blue solution of nitrogen dioxide–acetonitrile was introduced into the reaction mixture, after with oxygen was introduced at 100°C under a reaction pressure of 15 kg/cm². After few minutes of oxygen introduction, the absorption of oxygen began and some oxygenated products were obtained (Table 5). The distribution of these products was the same as Brill's[5)] and Imamura's[6)] reports. It is obvious that nitrogen dioxide initiates the reaction; this result corresponds to Titov's indication[7)]: nitrogen dioxide adds to the double bond of olefin and form a radical. If the bismuth nitrate thermally decomposes to give nitrogen dioxide, the autoxidation will be initiated by nitrogen dioxide. On the other hand, when glycerol (2.7 mol/l) was added to the solution on the oxidation of isobutene in the presence of the bismuth nitrate, the absorption of oxygen was suppressed and oxygen absorption was not observed until about 70 min after the introduction of the oxygen. The inhibiting effect of glycerol was examined at 70°C(Fig. 1). The rate of oxygen absorption decreased with the increase in the amount of glycerol added. However, the apparent absorption of oxygen was observed a few minutes after oxygen introduction on the oxidation of butene in the presence of nitrogen dioxide, and oxygenated products were obtained (Table 5). These results indicate that glycerol only disturbs the oxidation of isobutene in the presence of the bismuth nitrate and does not inhibit the oxidation initiated by nitrogen dioxide. Moreover, nitrogen dioxide was not observed experimentally on the oxidation of olefin in the presence of the bismuth nitrate(Table 3). If the nitrogen dioxide is formed from the bismuth nitrate, it should be effective for the oxidation of cumene, for it has been reported by Nanba *et al.*[8)] that nitrogen dioxide is able to abstract a hydrogen atom from cumene at 70°C. Judging from these results, it is difficult to take nitrogen dioxide as the active origin of the bismuth nitrate on the autoxidation of olefins. An oxygen atom in the triplet state is able to abstract hydrogen atom from hydrocarbons[9)] and to initiate the autoxidation. A singlet oxygen atom can not abstract a hydrogen atom from hydrocarbons, but it can give rise to insertion reaction.[10)] If the bismuth nitrate generates an oxygen atom by its thermal decomposition, the autoxidation of hydrocarbons will occur by hydrogen abstraction in case of the triplet oxygen atom generated. However, it is difficult to take the oxygen atom possibly generated from the nitrate as the active origin of the bismuth nitrate on the oxidation of olefins, because no catalytic effect of the bismuth nitrate was observed in the case of the oxidation of saturated hydrocarbons, such as cumene and tetralin (Table 2).

The effect of bismuth oxynitrate was examined by means of infrared absorption spectra. The IR spectra of the bismuth nitrate, $Bi(NO_3)_35H_2O$, is shown in Fig. 2; the characteristic absorption bands at 830, 1380, and 1620 cm^{-1} have been attributed to the modes of bending, stretching, and harmonics of the bending of the(N–O) bond respectively by Vratny.[11)] The

Table 5. The effect of NO_2 on the oxidation of butenes at 100°C

Olefins	Conv. of olefin[a)]	Absd. O_2[b)]	Products (mmol)				
			CH_3COCH_3	CH_3CHO	Epoxide	PO[c)]	Ester
iso-C_4H_8	24.4%	30.5 mmol	14.4		6.7	3.7	11.6
cis-2-C_4H_8	35.7	39.5		7.1	20.5	1.8	7.4
cis-2-C_4H_8[d)]	33.5	44.2		8.0	18.6	2.5	10.1

C_4H_8: 3.4 mol/l, NO_2: 0.34 mol/l, solvent: CH_3CN 50 ml, reaction time: 160 min.
a) Conversion of olefin. b) Absorbed oxygen. c) Peroxide. d) Glycerol (2.7 mol/l) was added.

---

6) J. Imamura, M. Hirata, I. Kawase, and N. Ohta, *Kogyo Kagaku Zasshi*, **68**, 2391 (1965).

7) A. I. Titov, *Tetrahedron*, **19**, 557 (1963).

8) T. Yoshida, F. Yamamoto, and K. Nanba, *Kogyo Kagaku Zasshi*, **73**, 519 (1970).

9) A. Kato and R. J. Cvetanović, *Can. J. Chem.*, **45**, 1845 (1967).

10) Y. Moro-oka, *Shokubai*, **13**, 135 (1971).

11) F. Vratny, *Appl. Spectrosc.*, **13**, 59 (1959).

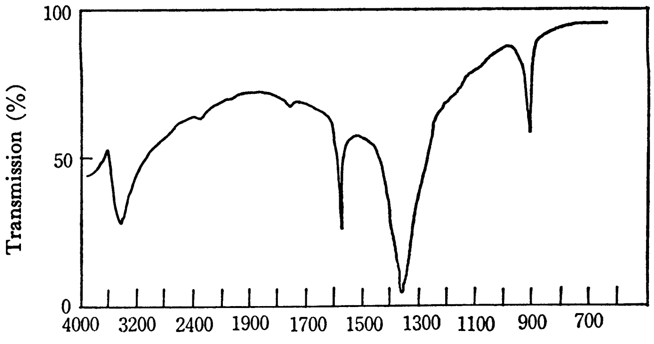

Fig. 2. Infrared spectra of $Bi(NO_3)_3 5H_2O$. Before use for reaction in KBr pellet.

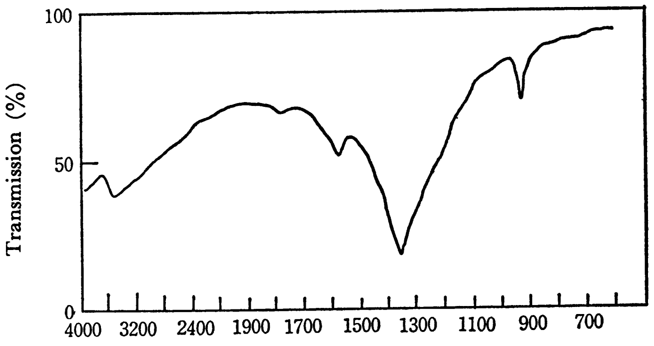

Fig. 3. Infrared spectra of white substance recovered from the reaction mixture.
100°C, 50 min, in KBr pellet.

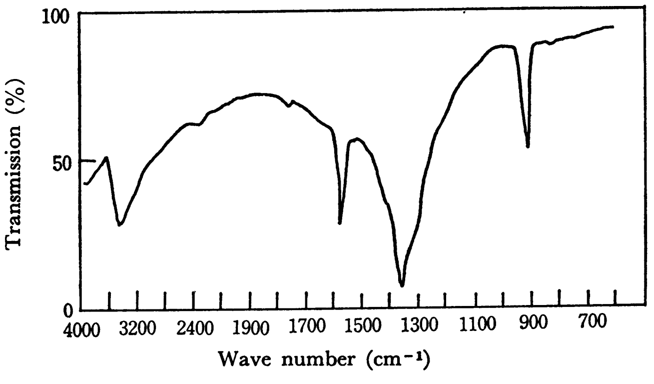

Fig. 4. Infrared spectra of $Bi(NO_3)_3 5H_2O$ treated in benzene at 80°C for 1 hr in KBr pellet.

absorption at 1620 cm^{-1} can also be attributed to the bending of H–O–H in the lattice. The IR spectra of the white substance recovered from the solution after a 50-min reaction using bismuth nitrate as the catalyst at 100°C are shown in Fig. 3. The absorptions at 830 and 1620 cm^{-1} decreased a little in their intensities, and the band at 1380 cm^{-1} became broad. However, the characteristic absorption were the same as those in Fig. 2. Cismaru *et al.*[12] indicate that the oxynitrate has split absorptions at 1320 and 1380 cm^{-1} as a result of an increase in the covalent bond-character of the (N–O) bond. Therefore, we can regard the recovered substance as a bismuth nitrate containing no bismuth oxynitrate. The spectra of the bismuth nitrate treated in benzene at 80°C for 1 hr were the same as those of the untreated one(Fig. 4). From these results, we can suppose that the bismuth nitrate is rather stable in circumstances, even if it is heated, and that the active origin of the bismuth nitrate is of itself.

cis-trans *Isomerization.* It has been reported in the previous paper[2] that the recovered *cis*-2-butene contained the *trans*-isomer after the oxidation of *cis*-2-butene at 100°C under a pressure of 20 kg/cm² in the presence of the bismuth nitrate. The isomerization of *cis*-2-butene was examined further in this paper. It was observed to take place in the presence of the bismuth nitrate with and without oxygen. It was also observed when nitrogen dioxide and bismuth trichloride were added; our findings are summarized in Table 6.

Glycerol did not prevent the isomerization so much, but it did prevent the oxidation. In the presence of glycerol, nitrogen dioxide promoted both the isomerization and the oxidation. The isomerization with the catalysts used here must be due to both protonic acid and to the coordinating of olefin to the bismuth

Table 6. Isomerization of *cis*-2-butene to *trans*-isomer

Catalyst	*cis*-/*trans*-2-C_4H_8 [a]	
—[b]	1/[c]	100°C
$Bi(NO_3)_3 5H_2O$	1/1.5	40°C without O_2
$Bi(NO_3)_3 5H_2O$	1/1.6	100°C with O_2
$Bi(NO_3)_3 5H_2O$-Glycerol	1/1.1	100°C with O_2
$Co(NO_3)_2 6H_2O$	1/0.9	100°C with O_2
NO_2	1/0.9	100°C with O_2
$BiCl_3$	1/0.8	100°C without O_2
$AlCl_3$	1/0[c]	100°C without O_2

cis-2-C_4H_8: 3.4 mol/l, solvent: CH_3CN, catalyst: 0.01 mol, reaction time: 160 min. 1-Butene was not observed in each case.
a) Molar ratio of *cis*-2-C_4H_8 to isomerized *trans*-isomer.
b) No catalyst was used. c) No isomerization was observed.

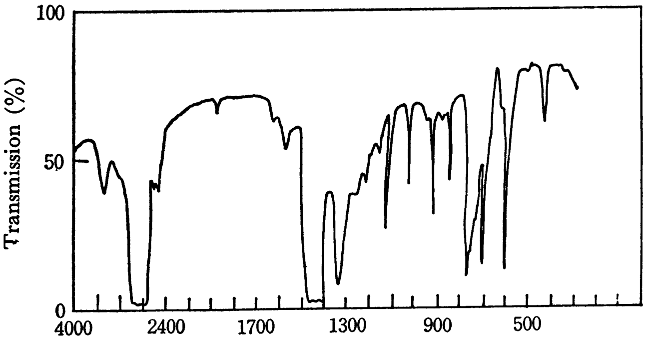

Fig. 5. Infrared spectra of $Bi(NO_3)_3 5H_2O$-cyclohexene solution. In Nujol. New absorptions were observed at 1880, 1000, 780, and 430 cm^{-1}.

---

[12] D. Cismaru, Z. Cimons and C. Volanschi, *Rev. Roum. Chem.*, **9**, 681 (1964); *Chem. Abstr.*, **62**, 14047a (1965).

[13] "Kagaku Benran Kisohen-1," Ed. by the Chemical Society of Japan, Maruzen, Tokyo (1966), p. 51.

nitrate. In the case of the oxidation, the coordination of olefin is probably prevented by the glycerol coordinated on the bismuth nitrate and the rate of oxidation is reduced. It can be assumed from above results that the initiation of the oxidation by the bismuth nitrate occurs by the direct interaction of the bismuth nitrate with olefin. The direct interaction was examined by studying the infrared spectra of the solution of bismuth nitrate–cyclohexene (Fig. 5). New bands, which were not observed on either the bismuth nitrate or cyclohexene, were observed at 430, 780, 1000, and 1880 cm^{-1}. Though the assignment of these bands is not clear, the newly-observed absorption, especially at 430 cm^{-1}, is significant because the absorption is near the characteristic absorption of Pt–C_2H_4(405 cm^{-1} in the Zeise salt. The coordination of cyclohexene is not clear in detail, but it is certain that the initiation of cyclohexene depends on this coordinated olefin. However, there is a possibility that a bismuth-oxygen complex may be formed during the reaction and that it contributes to the initiation by adding to the double bond of olefins. This possibility will be further investigated kinetically, and the direct interaction of the bismuth nitrate with olefin will be confirmed.