BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 312—318 (1969)

The Catalytic Activity of Onium Compounds in the Homogeneous Liquid Phase Oxidation of Cumene and α-Pinene

Kenichi FUKUI, Katsutoshi OHKUBO and Tokio YAMABE

Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

(Received May 29, 1968)

The catalytic activity of onium compounds was studied in the homogeneous liquid phase oxidation of cumene and α-pinene. The onium salts, particularly sulfonium, phosphonium, selenonium, arsonium and telluronium were found effective. This result is connected to the fact that the central atom in these onium has vacant d orbitals. Among the anions of the onium salts tested, phosphate and sulfate were most effective. The aryl substituents in the central sulfur in sulfonium lessened the activity, while alkyl substituents made it greater. These facts were attributed to charge migration from the substituents and the anionic part to the central atom.

In earlier papers,[1,2] it was reported that phosphonium and sulfonium halides were effective catalysts in the liquid phase oxidation of hydrocarbons such as tetralin, cumene and *p*-xylene, and that the activity of these catalysts was dependent upon the kind of halogen anions involved. Phosphonium and sulfonium tetrafluoroborates were not as effective as halides. Bredereck[3] also reported a similar effect of halogen anions in tetralin oxidation by several alkyl ammonium salts.

It was found later, however, that phosphate and sulfate anions of sulfonium salt were in some cases more active than halogen anions. In addition, the previous papers[1,2] had not discussed the effect of

---

[1] K. Fukui, K. Kanai, T. Takezono and H. Kitano, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **67**, 1131 (1964).

[2] K. Kanai, K. Ohkubo, H. Kitano and K. Fukui, *Bull. Japan Petr. Inst.*, **7**, 52 (1965).

[3] H. Bredereck, A. Wagner, R. Blascke, C. Demetriades and K. G. Kottenhahn, *Chem. Ber.*, **92**, 2628 (1959).

the structure of əɥı cation part of onium salts From this point, it was hoped to reinvestigate the catalytic activity of these onium salts in more detail.

It was attempted in the present paper to clarify mainly the role of the cation part of various onium salts in their catalytic action, in connection with the mechanism of interaction of onium catalysts with the oxygen molecule.

In order to investigate the effect of the cation part, the homogeneous liquid phase oxidation of cumene and α-pinene in the presence of tetrafluoroborates of the following oniums was carried out; carbonium, ammonium, oxonium, silyl, phosphonium, sulfonium, arsonium, selenonium and telluronium. The silyl compound was added to the group of onium compounds for comparison's sake. The central atoms of these oniums and their lowest vacant atomic orbitals which might play an important role in interaction with the oxygen molecule (discussed later) are listed in Table 1.

TABLE 1. THE LOWEST VACANT ATOMIC ORBITALS OF CENTRAL ATOMS OF ONIUM IONS

C (2p)	N (3s)	O (3s)
Si (3p)	P (4s, 3d)	S (4s, 3d)
	As (5s, 4d)	Se (5s, 4d)
		Te (6s, 5d, 4f)

It was found that, in these onium salts, phosphonium, sulfonium, selenonium, arsonium, and telluronium were effective; in particular, the first three were outstanding. These compounds are characterized in that the central atoms possess low-lying vacant d orbitals. The order of activity of these onium salts as compared with those with central atoms of elements in the same row of the periodic table was the following:

$$\text{carbonium} < \text{ammonium} < \text{oxonium}$$
$$\text{silyl} < \text{phosphonium} \simeq \text{sulfonium}$$
$$\text{arsonium } (\simeq \text{telluronium}) < \text{selenonium}$$

In order to investigate the effect of the anion part of onium salts, the oxidation of cumene was carried out with various triphenylsulfonium salts as catalysts, such as phosphate, sulfate, nitrate, chromate, perchromate, *etc.* It was found that triphenylsulfonium phosphate and sulfate were more effective than triphenylsulfonium halides in the initial step of oxidation. Furthermore, the effect of substituents of the cation part was investigated using a series of sulfonium tetrafluoroborates. Finally, the mechanism of this homogeneous oxidation with particular reference to the interaction between molecular oxygen nda catalysts was discussed.

Experimental

Material and Method of Oxidation. Cumene was washed with conc. sulfuric acid and dried with anhydrous magnesium sulfate, then distilled to collect the fraction (bp 152.0—152.5°C) which was used for oxidation. α-Pinene was distilled to obtain the 155—156°C fraction. The distillate (10 m*l*) was warmed in the presence of onium salts (0.03 mmol) to 85°C in a nitrogen atmosphere before charging with oxygen. The almost homogeneous solution obtained was subjected to oxidation with the same apparatus and in the same way as reported in a previous paper.[1)]

Catalysts. *Triphenylcarbonium Tetrafluoroborate.* Equimolar amounts of triphenylmethyl chloride and silver tetrafluoroborate were mixed in ethyl alcohol and stirred for about 5 hr to form a precipitate of silver chloride. After filtering the precipitate, the filtrate was evacuated to separate reddish yellow crystals of triphenylcarbonium tetrafluoroborate (yield 62%) melting at 207—210°C (dec.).

Found: C, 32.1; H, 6.29%. Calcd for $C_{18}H_{15}CBF_4$: C, 32.4; H, 6.10%.

Tetraethylammonium Tetrafluoroborate. After an equimolar mixture of triethyl amine and ethyl bromide was left standing for about a day in ethyl acetate, a precipitate of tetraethylammonium bromide was obtained, which was filtered and dried *in vacuo,* then, an equimolar mixture of tetraethylammonium bromide and silver tetrafluoroborate was similarly treated to obtain hygroscopic colorless crystals of tetraethylammonium tetrafluoroborate.

Found: C, 44.3; H, 9.22; N, 6.92%. Calcd for $C_8H_{20}NBF_4$: C, 44.2; H, 9.43; N, 6.79%.

Triphenyloxonium Tetrafluoroborate. Phenyldiazonium tetrafluoroborate (10. 5 g) and diphenyl ether (150 g) were refluxed in acetone (300 m*l*) at 80—90°C for half an hour and the solution quenched. The resulting precipitate was dried *in vacuo* to obtain colorless crystals (recrystallized from acetone and ether), melting range between 226 and 227°C (dec.).

Found: C, 28.3; H, 6.17%. Calcd for $C_{18}H_{15}OBF_4$: C, 28.5; H, 6.19%.

Triphenylsilyl Tetrafluoroborate. Tetrachlorosilane (5.7 g) was added to an ether solution of phenylmagnesium bromide (18.1 g) and the mixture refluxed to obtain colorless crystals of triphenylchlorosilane (90% yield), melting at 110—111°C, and equimolar quantities of triphenylchlorosilane and silver tetrafluoroborate were treated in the same way as mentioned above to obtain colorless crystals which were recrystallized from ether and ethyl acetate, mp 314—315°C.

Found: C, 62.4; H, 4.33%. Calcd for $C_{18}H_{15}SiBF_4$: C, 62.1; H, 4.35%.

Triphenylsulfonium-, Tetraphenylphosphonium-, Triphenylselenonium-, and Triphenyltelluronium Tetrafluoroborates. These onium salts were prepared by methods similar to those reported in a previous paper.[4)]

---

4) T. Hashimoto, M. Sugita, H. Kitano and K. Fukui, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **88**, 991 (1967).

Compound	Appearance	Mp (°C)	Found		Calcd	
			C (%)	H (%)	C (%)	H (%)
$(C_6H_5)_3S\text{-}\frac{1}{3}PO_4$	Colorless needles	201—201.5	72.2	5.09	72.0	5.11
$(C_6H_5)_3Se\text{-}\frac{1}{3}PO_4$	Colorless crystals	178—178.5	63.2	4.39	62.9	4.42
$(C_6H_5)_3Te\text{-}\frac{1}{3}PO_4$	Colorless crystals	240—240.5	60.5	4.20	60.1	4.41

Triphenylsulfonium-, Triphenylselenonium- and Triphenyltelluronium Phosphate. Twenty milliliters of an aqueous solution of potassium phosphate (0.4 mmol) were added to ethyl alcohol (200 *ml*) solutions of triphenylsulfonium, triphenylselenonium and triphenyltelluronium tetrafluoroborates (1 mmol), and the solutions kept standing for about 24 hr. The precipitates of potassium tetrafluoroborate were filtered off, and the filtrates evacuated in a nitrogen atmosphere. The raw crystals were recrystallized from chloroform and ether. Their appearances and analytical data are listed above.

Tetraphenylphosphonium and Triphenylsulfonium Chlorides. These chlorides were prepared as in previous papers.[1,5] Their appearances and analytical data are listed in the following.

Compound	Appearance	Mp (°C)	Found Cl (%)	Calcd Cl(%)
$(C_6H_5)_4PCl$	Colorless needles	271—272	9.6	9.5
$(C_6H_5)_3SCl$	Colorless needles	297—298	11.6	11.9

Tetraphenylarsonium Tetrafluoroborate. 41.9 g of tetraphenylarsonium chloride (colorless crystals melting at 256—257°C) and 19.47 g of silver tetrafluoroborate were treated similar to the sulfonium fluoroborates. Colorless crystals were obtained, melting at 318—319°C. Found: BF_4, 23.0%. Calcd for $C_{24}H_{20}AsBF_4$: BF_4, 23.4%.

Triphenylsulfonium Nitrate and Tetraphenylphosphonium Nitrate. These salts were prepared by a method similar to that given in a previous paper.[4] The former consisted of colorless needles melting at 225.5—226°C. (Found: C, 66.7; H, 4.71; N, 4.0%. Calcd for $C_{18}H_{15}SNO_3$: C, 66.4; H, 4.65; N, 4.3%), and the latter of colorless crystals melting at 283—284°C. (Found: C, 71.9; H, 5.1; N, 3.7%. Calcd for $C_{24}H_{20}PNO_3$: C, 71.8; H, 5.0; N, 3.5%.)

Triphenylsulfonium Salts. Triphenylsulfonium tetrafluoroborate and potassium salts were treated similar to triphenylsulfonium phosphate. The raw crystals were recrystallized from chloroform and ether. Triphenylsulfonium salts ($(C_6H_5)_3SX$) obtained are described below.

Alkyldiphenylsulfonium Tetrafluoroborate. Equimolar amounts of diphenyl sulfide and silver tetrafluoroborate were kept standing at room temperature to precipitate dark brown crystals which were dried *in vacuo*. Hygroscopic dark brown crystals of diphenyl sulfide-silver fluoroborate complex (90% yield) were obtained which melted at 54—55°C (dec.). (Found: C, 38.5; H, 2.5%. Calcd for $C_{12}H_{10}SBF_4Ag$: C, 37.9; H, 2.6%.) Alkyl iodide (0.08 mol) was added to an ethylene chloride solution of the complex (0.056 mol). The solution was stirred for *ca.* 2 hr at room temperature and left standing overnight to precipitate silver iodide which was removed. After the solvent was removed from the nitrogen atmosphere, crystals were obtained which were recrystallized from chloroform and ether. The products are listed below.

$(C_6H_5)_2RSBF_4$ R	Yield (%)	Mp (°C)	BF_4 Found (%)	Calcd (%)
CH_3	44	61—62	30.5	30.9
C_2H_5	40	76—77	28.8	29.4
$n\text{-}C_3H_7$	41	115.5—116.5	27.5	27.7
$n\text{-}C_4H_9$	40	85—86	26.3	27.1

Trialkylsulfonium Tetrafluoroborates. These salts were prepared by the same method as in a previous paper.[5] Analytical data are as follows: $(CH_3)_3SBF_4$ melting at 307—308°C (dec.) (Found: BF_4, 52.3%, Calcd for $C_3H_9SBF_4$: BF_4, 52.9%) and $(C_2H_5)_3SBF_4$ melting at 104—105°C (Found: BF_4, 43.4%, Calcd for $C_6H_{15}SBF_4$: BF_4, 42.1%).

Benzylmethylphenylsulfonium and Dibenzylmethylsulfonium Tetrafluoroborates. Methyl iodide (0.08 mol) was added

$(C_6H_5)_3SX$ X	Appearance	Mp (dec.) (°C)	Found		Calcd	
			C (%)	H (%)	C (%)	H (%)
$\frac{1}{2}SO_4$	Colorless needles	178—179	69.4	4.82	69.7	4.90
$\frac{1}{2}CrO_4$	Colorless needles	181.5—182	67.3	4.67	67.0	4.65
$\frac{1}{2}Cr_2O_7$	Yellow crystals	228.5—239	58.3	4.05	58.7	4.65
$\frac{1}{3}Fe(CN)_6$	Pale green crystals	189—190	71.9	4.49	72.2	4.39
$\frac{1}{2}Ni(CN)_4$	Colorless crystals	164.5—165	68.9	4.31	69.1	4.33
$\frac{1}{2}SeO_4$	Colorless crystals	110—110.5	64.0	4.49	64.4	4.52
$\frac{1}{2}TeO_4$	Colorless needles	191—192	60.0	4.15	60.1	4.21
$\frac{1}{4}P_2O_7$	Colorless needles	190.5—191	70.1	4.81	70.4	4.85
$\frac{1}{2}CO_3$	Colorless needles	189—189.5	75.3	5.52	75.9	5.33

---

[5] K. Fukui, K. Kanai and H. Kitano, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **82**, 178 (1961).

to an ethylene chloride solution of equimolar (0.056 mol) amounts of silver tetrafluoroborate and benzylphenylsulfide or dibenzylsulfide. The mixture was treated similar to alkyldiphenylsulfonium tetrafluoroborate, and the following sulfonium tetrafluoroborates obtained: $C_6H_5CH_2(CH_3)(C_6H_5)SBF_4$ melting at 126.5—127.5°C (Found: BF_4, 28.6%. Calcd for $C_{14}H_{15}SBF_4$: BF_4, 29.1%) and $(C_6H_5CH_2)_2CH_3SBF_4$ melting at 214—215°C. Found: BF_4, 29.1%. Calcd for $C_{13}H_{17}SBF_4$: BF_4, 29.7%.

Phenyl-bis-(p-fluorophenyl) sulfonium Tetrafluoroborate. Equimolar quantities of phenylmagnesium bromide and di-*p*-fluorophenylsulfoxide were refluxed in benzene for *ca.* 2 days to precipitate phenyl-bis-(*p*-fluorophenyl) sulfoxymagnesium bromide. The precipitates were triturated with 20% hydrogen tetrafluoroborate and after extraction of the benzene phase by chloroform, followed by the removal of chloroform and recrystallization from chloroform and ether, colorless crystals of phenyl-bis-(*p*-fluorophenyl) sulfonium tetrafluoroborate were obtained, melting at 185—186°C. Found: BF_4, 22.1%. Calcd for $C_{18}H_{13}SBF_6$: BF_4, 22.5%.

Tribenzylsulfonium Tetrafluoroborate. An equimolar mixture of benzylmagnesium bromide and dibenzylsulfoxide was refluxed in benzene and treated similar to phenyl-bis-(*p*-fluorophenyl)sulfonium tetrafluoroborate. Colorless crystals of tribenzylsulfonium tetrafluoroborate were obtained. Mp 177.5—178.5°C. Found: BF_4, 21.8%. Calcd for $C_{21}H_{21}SBF_4$: BF_4, 22.1%.

Results

The Effect of the Central Atom of the Onium Cation. In order to investigate the effect of a difference in nature of the central atom of the onium cation, the liquid phase oxidation of cumene and α-pinene (10 m*l*) was carried out at 85°C in the presence of 0.03 mmol of triphenyl- or tetraphenylonium tetrafluoroborate (except for ammonium, where the tetraethyl derivative was taken), and the amounts of the following main products were determined; cumene hydroperoxide (CHP), dicumyl peroxide (DCP), acetophenone (AP) and α-cumyl alcohol (α-CA) in cumene oxidation products, and hydroperoxides (HPO) containing myrtenyl-, verbenyl- and pinocarveyl hydroperoxides and verbenone (VN) in α-pinene oxidation products. Catalysts used and oxidation products are listed in Tables 2 and 3.

TABLE 2. THF EFFECT OF THE DIFFERENCE IN THE ONIUM CENTRAL ATOM ON CUMENE OXIDATION
(Reaction temp.: 85°C, Reaction time: 4.0 hr)

Catalyst	O_2 absorbed (mmol)	$Rate_{max} \times 10^4$ $(mol \cdot l^{-1} \cdot sec^{-1})$	CHP (%)
$(C_6H_5)_3CBF_4$	2.11	0.26	99.4
$(C_2H_5)_4NBF_4$	4.16	0.34	99.5
$(C_6H_5)_3OBF_4$	5.97	0.67	93.7
$(C_6H_5)_3SBF_4$	10.45	1.12	99.5
$(C_6H_5)_3SeBF_4$	10.35	1.04	99.8
$(C_6H_5)_3TeBF_4$	3.85	0.45	99.7
$(C_6H_5)_4AsBF_4$	2.20	0.22	99.8
none	1.87	0.17	99.5

TABLE 3. THE EFFECT OF THE DIFFERENCE IN THE ONIUM CENTRAL ATOM ON α-PINENE OXIDATION
(Reaction temperature: 85°C)

Catalyst	Reaction time (hr)	O_2 absorbed (mmol)	$Rate_{max} \times 10^4$ $\left(\begin{matrix} mol \cdot l^{-1} \cdot \\ sec^{-1} \end{matrix}\right)$	HPO (%)
$(C_6H_5)_3CBF_4$	2.0	3.47	0.52	64.6
$(C_2H_5)_4NBF_4$	2.0	3.86	0.74	61.5
$(C_6H_5)_3OBF_4$	2.0	4.0	0.82	63.4
$(C_6H_5)_3SiBF_4$	2.0	4.24	0.75	99.9
$(C_6H_5)_4PBF_4$	2.0	4.58	0.89	100
$(C_6H_5)_3SBF_4$	2.0	5.82	0.97	99.9
none	3.0	3.21	0.34	31.2

In these and subsequent tables, the percentage of a product (for instance, CHP (%) in Table 2) is defined by

$$\frac{\text{moles of the product cocerned}}{\text{total moles } O_2 \text{ absorbed}} \times 100$$

But in the case of DCP (%), the percentage is defined by

$$\frac{2 \times \text{moles of the product concerned}}{\text{total moles } O_2 \text{ absorbed}} \times 100$$

All products were analyzed according to a procedure similar to that described in the preceding paper. Since all products except DCP mentioned here are formed in the equimolar consumption of oxygen molecules, the total sum of such percentages must be nearly one hundred, as seen in each table.

The approximate order of catalytic activity of these onium tetrafluoroborates was determined as the combined results of cumene and α-pinene oxidations as follows: carbonium$<$ammonium$<$oxonium, silyl$<$phosphonium$<$sulfonium, arsonium$\simeq$telluronium$<$selenonium. This order was defined by the total sum of oxygen absorbed which almost paralleled the maximum reaction rate at the propagation step, as seen in Tables 2 and 3.

In order to investigate further the effect of the cation central atom, the oxidation of cumene (10 m*l*) was carried out in the presence of tetraphenylphosphonium nitrate and triphenylsulfonium nitrate (0.03 mmol), and α-pinene (10 m*l*) oxidation by triphenylsilyl, tetraphenylphosphonium, triphenylsulfonium and tetraphenylarsonium chlorides (0.03 mmol). The results are listed in Tables 4 and 5.

The oxidation of cumene (10 m*l*) was also carried out with triphenylsulfonium triphenylselenonium and triphenyltelluronium phosphates (0.03 mmol). The results are presented in Table 6.

In these phosphates, the order of activity was found to be the following: sulfonium$>$selenonium$>$telluronium. As seen in Table 6, phosphates exhibited remarkable activity in oxygen absorption.

TABLE 4. CUMENE OXIDATION IN THE PRESENCE OF TETRAPHENYLPHOSPHONIUM AND TRIPHENYLSULFONIUM NITRATES
(Reaction temp.: 85°C, Reaction time: 4.0 hr)

Catalyst	O_2 absorbed (mmol)	CHP (%)	AP (%)
$(C_6H_5)_4PNO_3$	7.04	99.6	0.40
$(C_6H_5)_3SNO_3$	7.08	97.3	0.64
none	1.87	99.5	

TABLE 5. α-PINEN OXIDATION IN THE PRESENCE OF ONIUM CHLORIDES AT 85°C

Catalyst	Reaction time (hr)	O_2 absorbed (mmol)	HPO (%)
$(C_6H_5)_3SiCl$	2.3	6.32	57.0
$(C_6H_5)_4PCl$	2.5	9.33	49.8
$(C_6H_5)_3SCl$	2.5	9.75	48.2
$(C_6H_5)_4AsCl$	2.5	4.62	59.8
none	3.0	3.21	31.2

TABLE 6. CUMENE OXIDATION WITH ONIUM PHOSPHATES AT 85°C (Reaction time 4.0 hr)

Catalyst	O_2 absorbed (mmol)	CHP (%)	AP (%)	DCP (%)	α-CA (%)	Total (%)
$(C_6H_5)_3S$-⅓PO_4	19.5	64.0	3.92	trace	32.0	99.0
$(C_6H_5)_3Se$-⅓PO_4	18.1	79.5	2.38	trace	18.1	99.9
$(C_6H_5)_3Te$-⅓PO_4	4.1	100				100
none	1.87	99.1				

Such an effect of the anion part was re-examined in succeeding experiments.

The Effect of Anion Part. A series of triphenylsulfonium (0.03 mmol) with various anion parts was employed for cumene (10 m*l*) oxidation. The results are given in Table 7.

Also, the oxidation of α-pinene (10 m*l*) with triphenylsulfonium sulfate, selenate, and tellurate (0.03 mmol) was carried out. As seen in Table 8, the activity was found to be in the following order: $SO_4^{2-} > SeO_4^{2-} > TeO_4^{2-}$.

TABLE 7. THE EFFECT OF THE ANION PART UPON CUMENE OXIDATION IN TRIPHENYLSULFONIUM SALT CATALYSTS
(Reaction temp.: 85°C, Reaction time: 4.0 hr)

Catalyst Anion	O_2 absorbed (mmol)	CHP (%)	DCP (%)	AP (%)	α-CA (%)	Total (%)
⅓PO_4	19.5	64.0	trace	3.92	32.0	99.9
½SO_4	6.56	99.1	trace	0.90	trace	100
½CrO_4	8.10	89.0	8.02	2.84	trace	100
½Cr_2O_7	6.92	81.0	1.45	3.08	10.5	96.0
⅓$Fe(CN)_6$	3.52	99.9	trace	trace	trace	99.9
½$Ni(CN)_4$	8.56	72.4				
¼P_2O_7	14.8	89.6				
½CO_3	9.65	86.5	11.0	2.32	trace	99.8
NO_3	7.08	99.6				
IO_3	10.15	74.8	22.7	2.16	trace	98.9
ClO_3	0.51	98.0				
Cl	4.88	41.0	1.74	16.7	21.5	96.6
uone	1.87	99.5				

TABLE 8. THE OXIDATION OF α-PINENE WITH TRIPHENYLSULFONIUM SULFATE, SELENATE, AND TELLURATE
(Reaction temp.: 85°C, Reaction time: 2.0 hr)

Catalyst	O_2 absorbed (mmol)	HPO (mmol)	HPO (%)	VN (mmol)	VN (%)
$(C_6H_5)_3S$-½SO_4	22.2	8.0	36.3	5.25	23.6
$(C_6H_5)_3S$-½SeO_4	13.2	5.30	40.1		
$(C_6H_5)_3S$-½TeO_4	4.23	3.0	71.0		
none*	3.21	1.00	31.2		

* Reaction time was 3.0 hr.

The Effect of Substituents of the Onium Cation. It is of interest to examine the effect of substituents of the onium cation in connection with knowledge on the nature of the reaction mechanism. The oxidation of α-pinene (10 m*l*) was carried out with sulfonium tetrafluoroborates (0.03 mmol) with

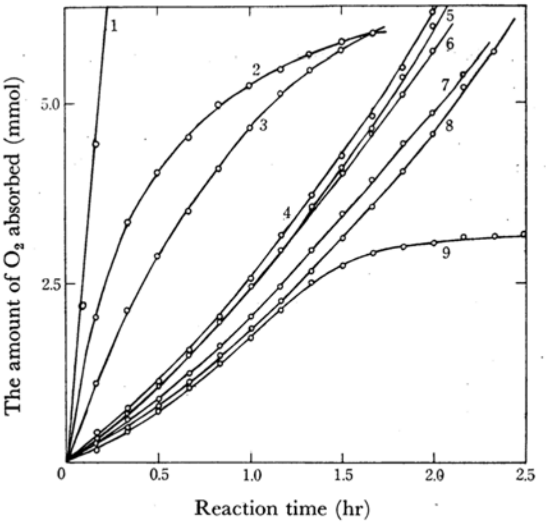

Fig. 1. The oxygen absorption curve of α-pinene the presence of sulfonium tetrafluoroborate (R_1-(R_2)(R_3)SBF_4).

	1	2	3	4	5
R_1	C_2H_5	$C_6H_5CH_2$	CH_3	$C_6H_5CH_2$	$C_6H_5CH_2$
R_2	C_2H_5	$C_6H_5CH_2$	CH_3	$C_6H_5CH_2$	C_6H_5
R_3	C_2H_5	$C_6H_5CH_2$	CH_3	CH_3	CH_3

	6	7	8	9
R_1	C_6H_5	CH_3	C_6H_5	none
R_2	C_6H_5	C_6H_5	*p*-F–C_6H_4	
R_3	C_6H_5	C_6H_5	*p*-F–C_6H_4	

different alkyl or aryl substituents on the sulfur atom. The results are shown in Fig. 1. As shown in Fig. 1, the more aryl substituents attached to the sulfur atom, the lower the activity became.

The oxidation of α-pinene (10 m*l*) was also carried out with alkyldiphenylsulfonium tetrafluoroborates (0.03 mmol) in which the alkyl was methyl, ethyl, *n*-propyl or *n*-butyl at 85°C for 2.5 hr. The results given in Table 9 show that the larger the alkyl group, the higher the catalytic activity became.

The present reaction is a liquid phase (essentially homogeneous) oxidation in which the catalyst structure can be systematically varied, if desired. An investigation of the relation between the structure and the activity of catalysts is expected to supply a clue to the reaction mechanism on a molecular level. It is stressed in this connection that these onium catalysts are, in general, thermally stable and are little oxidized by oxygen molecules, so that we might conclude that they would not act as radical sources in these homogeneous liquid phase oxidations.*1

Discussion

Tables 2 and 3 indicate that the onium salts in which the central atoms are S, Se, Te, P and As are effective catalysts in the liquid phase oxidation of cumene and α-pinene. These atoms are characterized by the fact that they possess vacant d orbitals not far above their valence shells. In view of the widely known participation of d-orbital expansion in the chemistry of sulfur or related atom compounds,[6] it may be worth-while to examine the possibility of relating the outstanding activity of the onium salts to the interaction of their d orbitals.

The electronic state of the onium ion may be thought to be such that the electrons in surrounding alkyl or aryl groups are partially transfered to the spacially far-reaching vacant d orbitals, the energy of which is considerably lowered by the positive charge of the central atom. It is also probable that the anion might take part in this interaction since the "bond" between the anion and the cation part might reasonably be considered to have a more or less covalent nature.

The positive charge on the central atom may thus be partially neutralized by an inflowing electronic charge, and consequently the vacant d orbitals become partially occupied. The resulting electronic state of the onium central atom will, in part, resemble that of the transition metal atoms bearing d electrons properly and exhibiting a variety of catalytic activities in many heterogeneous catalyses.

In this connection, it is of interest to inspect the possibility of interaction between the "partially occupied" d orbital at the onium center considered above and the half-occupied, doubly-degenerate $1\pi_g$ molecular orbitals of the ground-state ${}^3\Sigma_g^-$ oxygen molecule. A mode of interaction will become probable when the orbital symmetry relationship becomes favorable.[7]

The circumstances are illustrated in Fig. 2, where the mode of interaction of the oxygen molecule is assumed parallel to the ligand plane. The d orbitals which can be utilized for interaction with O_2 are d_{xy} and d_{xz}. The latter, being of lower energy, would be able to partake in dp–σ type bonding through favorable orbital overlapping. The former d orbital will concern a more labile bond of a dp–π type, also contributing to the bonding interaction between onium and oxygen.

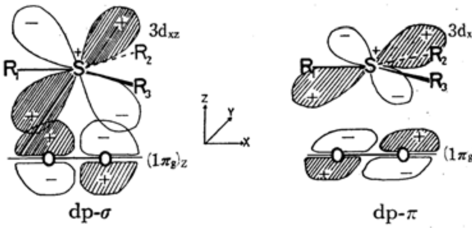

Fig. 2. The interaction between 3d orbital of sulfonium and $1\pi_g$ molecular oxygen.

First comes the depression of catalyst activity by the coexistence of a certain group of compounds which might be thought to possess a stronger affinity to sulfonium salts than molecular oxygen. It is well known[8] that sulfonium halides form stable trihalides in the presence of halogen molecules. Triphenylsulfonium iodide (mp 214—215°C (dec.)) or tetraphenylphosphonium bromide (mp 288—289°C (dec.)) does not initiate cumene oxidation at all at 85°C when used with an equimolar amount of iodine. Also, oxidation proceeding with these sulfonium halides stops completely upon the addition of equimolar iodine. Triphenylsulfonium

---

[*1] In fact, more than 70% of catalysts were recovered from the reaction mixtures, and no appreciable amount of decomposed or oxidized products of catalysts was detected by gas chromatography. Triphenylsulfonium tetrafluoroborate decomposed gradually at 300—350°C to produce fluorobenzene, diphenylsulfide and boron trifluoride. But under the reaction conditions in the present paper, neither sulfide, sulfoxide nor fluorobenzene was detected by gas chromatography. The deactivation of catalysts by the addition of oxidation products was observed, which will be discussed in detail in a subsequent paper.

6) G. Cilento, *Chem. Revs.*, **60**, 147 (1960).

7) K. Fukui, This Bulletin, **39**, 498 (1966) and references cited therein.

8) K. Kanai, T. Hashimoto, H. Kitano and K. Fukui, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **86**, 534 (1965).

triiodide (brown crystals, mp 137—138°C) and tetraphenylphosphonium diiodobromide (brown crystals, mp 249—250.5°C) exhibited no activity as catalysts for cumene oxidation.

Such a remarkable deactivation is also seen in the employment of solvents bearing lone-pair electrons. Chloroform, dioxane or acetic acid used as solvent causes the activity of triphenylsulfonium salts to completely disappear. These results might come from the blocking effect of these additives against the interaction of the sulfur d orbital with molecular oxygen.

TABLE 9. α-PINENE OXIDATION BY THE USE OF ALKYL DIPHENYLSULFONIUM TETRAFLUOROBORATE
(Reaction temp.: 85°C, Reaction time: 2.5 hr)

Catalyst	O_2 absorbed (mmol)	HPO (mmol)	HPO (%)	VN (mmol)	VN (%)
$CH_3(C_6H_5)_2SBF_4$	6.37	5.15	80.8	0.56	8.78
$C_2H_5(C_6H_5)_2SBF_4$	6.96	5.05	72.5	0.85	12.2
n-$C_3H_7(C_6H_5)_2SBF_4$	7.04	4.10	58.3	0.92	13.1
n-$C_4H_9(C_6H_5)_2SBF_4$	7.92	4.20	53.0	1.02	13.9
none*	3.12	1.00	31.2	0.69	21.5

* Reaction time was 3.0 hr.

As understood from Fig. 1 and Table 9, the catalytic activity is affected by substituents on the sulfur atom. The mode of partial occupation of d orbital mentioned above may be influenced by substituents. The charge of a d orbital will be increased by electron-donor groups like methyl, ethyl, or larger alkyls attached to the central atom, whereas it will be decreased by such groups as phenyl or *p*-fluorophenyl, so that the interaction of a d orbital with an oxygen molecule may be weakened.

Second, the effect of the anion part should be mentioned. The tetrafluoroborates of such oniums as carbonium, ammonium and oxonium are less active than other onium salts mentioned above. This is probably because their ionic character is too large to transfer electrons from anion to onium, so that interaction between their vacant orbitals and molecular oxygen orbitals is only slight.

In this connection, it is interest to see the relation between the pK_1 value of the acid corresponding to the anion and catalytic activity. An apparent correlation is found in Fig. 3. A suitable range of acidity seems to exist, corresponding to a suitable range of covalent nature of the "bond" between the onium and anion parts.

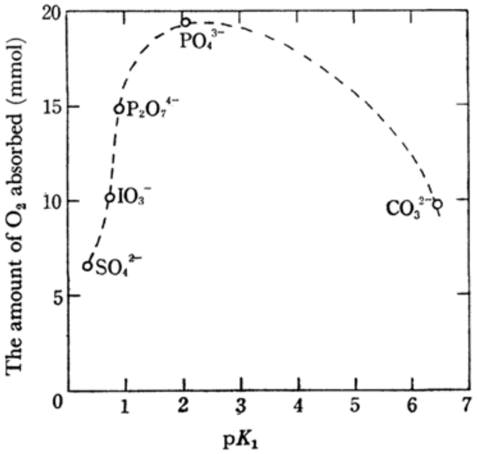

Fig. 3. The effect of pK_1 of the acid corresponding to the anion upon the catalytic activity of triphenylsulfonium salts.

Third, it should be noted that kinetic investigation also seems to favor the molecular oxygen association mechanism, the details of which will be reported in a subsequent paper. The reaction scheme required to satisfy the experimental results involves the interaction of molecular oxygen with the catalyst molecule.

Part of the cost of this investigation was defrayed by a Scientific Research Grant from the Ministry of Education, to which the authors' thanks are due.