Fluorides of group V and VI elements as new catalysts for the reaction of CO_2 with oxiranes

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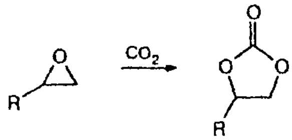
Organoelement fluorides of group V and VI elements were found to be efficient catalysts for the synthesis of cyclic carbonates from oxiranes and CO_2.

Key words: carbon dioxide, cyclic carbonates, organoelement fluorides.

The problem of activation and chemical binding of carbon dioxide is of increasing interest because of the unfavorable climatic changes resulting from global warming.[1,2] The current ways of utilizing CO_2 can be divided into two large groups, *viz.*, reduction to hydrocarbons (fuel regeneration) and use in organic synthesis as an available C_1 synthon. The former group is not promising because fuel is burnt to give CO_2 again. As for the latter,[3,4] it appears quite useful to bind CO_2 in polymers, which take carbon dioxide out of the cycle for a long period of time.

Actually, a sole reaction performed industrially is the addition of CO_2 to oxiranes to give alkylene carbonates and their subsequent polymerization (Eq. (1)).



(1)

This reaction is known to occur as a catalytic process. Many types of catalysts, *e.g.*, porphyrin and phthalocyanine complexes of metals,[5—9] complexes of organotin iodides with phosphines;[10,11] complexes of copper(I) with isocyanides;[12] ammonium, phosphonium, and sulfonium salts;[13] and alkali and alkaline-earth metal halides[14] have been studied. These systems differ strongly in catalytic activity: some porphyrin complexes in combination with *N*-methylimidazole allow one to obtain carbonates in satisfactory yield at room temperature and atmospheric pressure, while salt catalysts require long (tens of hours) heating at 150—200 °C and 50—100 atm. The drawback to the metallocomplex catalysts is that it is difficult to prepare them and, in the case of copper and tin complexes, they are not quite chemically stable. With the aim of searching for new efficient and available catalysts for performing this reaction, we studied fluorides of group V and VI elements, *viz.*, Ph_3SbF_2, Ph_3BiF_2, SbF_3, $PhTeF_3$, and $PhTeF_5$ in the synthesis of propylene carbonate (R = Me) from CO_2 and propylene oxide (Table 1).

Results and Discussion

An analysis of the literature data showed that an efficient catalyst should have the properties of both a

Table 1. Yield of propylene carbonate depending on the catalyst and the reaction conditions

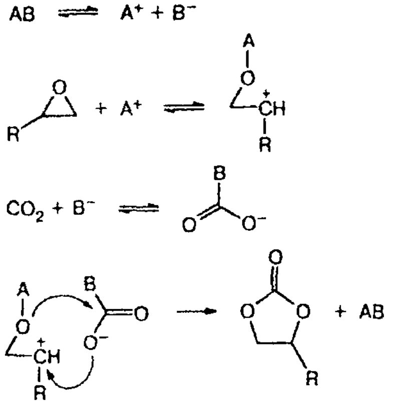
Run	Catalyst	T/°C	t/h	Additive	Yield (%)
1	Ph_3SbF_2	180	2	HMPA[a]	25
2	Ph_3SbF_2	180	5.5	HMPA	100
3	Ph_3SbF_2	180	2	—	0
4	Ph_3SbF_2	180	2	Pyridine	72
5	Ph_3SbF_2	180	2	MeCN	0
6	Ph_3SbF_2	140	5.5	HMPA	8
7	Ph_3BiF_2	180	2	—	0
8	Ph_3BiF_2	180	2	HMPA	12.5
9	SbF_3	180	2	HMPA	7
10	$PhTeF_3$[b]	140	5	HMPA	90
11	$PhTeF_3$	140	5	Pyridine	100
12	$PhTeF_5$	180	2	HMPA	100
13	$PhTeF_5$	140	5	HMPA	73
14	$PhTeF_5$	180	2	—	0.3
15	SbF_5	20		HMPA	Polymer
16	CsF	180	2	HMPA	4
17	—	180	2	HMPA	3
18	—	180	2	Pyridine	0
19	—[b]	180	2	HMPA	4

[a] Hexamethylphosphortriamide (hexametapol).
[b] Epichlorohydrin was used as a substrate.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1649—1651, August, 1998.

weak acid (for electrophilic activation of the oxirane ring) and a weak base (for nucleophilic activation of CO_2) (Scheme 1). It is necessary that the acid and the base be weak, since a strong acid will initiate fast polymerization of oxirane, and a strong base will irreversibly bind CO_2 into a carbonate.

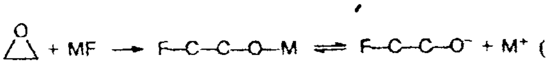
Scheme 1



Usually, a catalyst's cation serves as a Lewis acid, while both a catalyst's anion and alkoxides resulting from the oxirane ring opening can serve as a base B^- (for example, ω-chloroalkoxides $Cl—CH_2CH_2—O—CH_2CH_2—O—AlX_2$ are obtained from ethylene oxide and complex aluminum chlorides [6]).

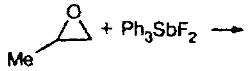
It was found that the fluorides themselves (which probably only slightly dissociate under the reaction conditions) do not manifest catalytic activity (runs *3*, *7*, and *14*), but on addition of solvents that facilitate ionic dissociation (pyridine or HMPA) they acquire high activity in certain cases. We found that the fluoride ion in the presence of weakly electrophilic cations almost does not exhibit catalytic activity (runs *9* and *16*). In contrast, SbF_5, a very strong Lewis acid, initiates the polymerization of oxirane even in combination with HMPA (run *15*). This reaction is competitive and, in the case of highly electrophilic cations, reduces the product yield. The bases themselves (HMPA and pyridine) in the absence of an acid component catalyze the reaction only slightly if at all (runs *17*—*19*).

We assume that β-fluoroalkoxide resulting from electrophilic opening of the oxirane ring (Eq. (2)) can serve as a base.



(2)

To check this assumption, we carried out the reaction of propylene oxide with Ph_3SbF_2 in the absence of CO_2 and, in fact, the formation of fluoroalkoxide anions was detected by ^{19}F NMR spectroscopy (Eq. (3)).



$$\longrightarrow FCH_2CH(Me)OSbFPh_3 + MeCHFCH_2OSbFPh_3 \quad (3)$$

The ^{19}F NMR spectrum of the reaction mixture contains two groups of signals ($CDCl_3$, CF_3COOH), δ, *J*: −150.8 (td, $FCH_2CH—$, $^2J_{F,H}$ = 50.5 Hz, $^3J_{F,H}$ = 17 Hz) and −111.2 (m, $FCH(Me)CH_2—$, $^3J_{F,H}$ = 24 Hz) (*cf.* Ref. 15).

In addition, the fluorocarbonate anion resulting from the reaction of fluoride with CO_2 (Eq. (4)) can also serve as a base. We did not observe an absorption band of $FCOO^-$ in the IR spectrum of a mixture CsF, HMPA, and CO_2, which however does not exclude its possible formation under the reaction conditions, *viz.*, at high temperature (140—180 °C) and a CO_2 pressure 70—100 atm.

$$CO_2 + F^- \rightleftharpoons FCOO^- \quad (4)$$

We believe that the Lewis acidity is the most important factor in the series of catalysts studied by us. This should be insufficient to induce polymerization of oxiranes but as high as possible for efficient opening of the epoxy ring.

Comparison of the activity of the catalysts studied by us with the patented ones [8,9,14] shows that some fluorides exceed the known catalysts (except for porphyrin ones) in parameters, and are much more easily available.

Experimental

Organoelement fluorides were synthesized according to the known procedures.[16—18] CsF and SbF_3 were ignited in the vacuum of an oil pump at 200 and 100 °C, respectively. Pyridine and hexametapol were distilled over alkali. SbF_5 was not purified. Both commercial-grade carbon dioxide (without additional purification) and that dried by passing through three successively connected washers filled with conc. H_2SO_4 were used in runs *1*, *2*, and *11* (see Table 1), the yields in both cases differing by no more than 2%. In all the other cases, commercial-grade CO_2 was used without additional purification. Propylene oxide (Merck) was preliminarily distilled over solid KOH. Epichlorohydrin (Fluka) was used without additional purification. Products were analyzed by column chromatography on a Chrom-5 instrument using the SE-30 phase. ^1H and ^{19}F NMR spectra were recorded on a Bruker CXP-200 spectrometer (200 and 188 MHz, respectively).

Propylene oxide (2.05 g, 2.5 mL, 36 mmol), a catalyst (250—300 mg), and a polar aprotic solvent (0.4 mL) were placed into a steel autoclave (50 mL). The autoclave was hermetically sealed, filled with carbon dioxide under a pressure of 50 atm, and placed into a thermostat. After a definite period of time, the autoclave was cooled, and the excess of CO_2 was removed. The reaction mixture was dissolved in 10 mL of dry CH_2Cl_2, the total volume was brought up to 15 mL, and the mixture was analyzed by GLC using a calibration curve. Propylene carbonate obtained (b.p. 237—238 °C (*cf.* Ref. 7: b.p. 240 °C)) was used for calibration. ^1H NMR ($CDCl_3$), δ:

1.45 (d, 3 H, Me, ^3J = 6.2 Hz); 4.00 and 4.51 (dd and t, 1 H and 1 H, CH_2, AB part of the ABX system, $^2J_{AB}$ = 8 Hz, $^3J_{AX}$ = 7 Hz, and $^3J_{BX}$ = 8 Hz); 4.84 (m, 1 H, CH).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-33060) and the Foundation for Support of Young Scientists of the Russian Academy of Sciences.

References

1. M. Aresta, E. Quaranta, and I. Tommasi, *New J. Chem.*, 1994, **18**, 133.
2. R. Quinn, J. B. Appleby, and G. P. Pez, *J. Am. Chem. Soc.*, 1995, **117**, 329.
3. T. Tsuda, *Gazzetta Chimica Italiana*, 1995, **125**, 101.
4. A. Behr, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 661.
5. W. J. Kruper and D. V. Dellar, *J. Org. Chem.*, 1995, **60**, 725.
6. T. Aida and S. Inoue, *J. Am. Chem. Soc.*, 1983, **105**, 1304.
7. K. Kasuga, S. Nagao, T. Fukumoto, and M. Handa, *Polyhedron*, 1996, **15**, 69.
8. US Pat. 4.663.467.
9. US Pat. 5.283.356.
10. I. Shibata, A. Baba, H. Iwasaki, and H. Matsuda, *J. Org. Chem.*, 1986, **51**, 2177.
11. A. Baba, K. Seki, and H. Matsuda, *J. Heterocycl. Chem.*, 1990, **27**, 1925.
12. T. Tsuda, Y. Chujo, and T. Saegusa, *J. Am. Chem. Soc.*, 1980, **102**, 431.
13. US Pat. 4.786.741.
14. Eur. Pat. Off. 0297647.
15. S. A. Lermontov, S. I. Zavorin, I. V. Bahtin, N. S. Zefirov, and P. J. Stang, *Phosphorus, Sulfur, and Silicon*, 1995, **102**, 283.
16. L. M. Yagupol'skii, V. I. Popov, N. V. Kondratenko, B. L. Korsunskii, and N. N. Aleinikov, *Zh. Org. Khim.*, 1975, **11**, 459 [*J. Org. Chem. USSR*, 1975, **11** (Engl. Transl.)].
17. K. Alam and A. F. Janzen, *J. Fluor. Chem.*, 1985, **27**, 467.
18. S. A. Lermontov, I. M. Rakov, N. S. Zefirov, and P. J. Stang, *Tetrahedron Lett.*, 1996, **37**, 4051.

Received October 10, 1997;
in revised form March 27, 1998

The use of hexafluoropropene oxide in substitutive fluorination of Sb^V and Bi^V oxygen-containing compounds

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Reactions of hexafluoropropene oxide with Sb^V and Bi^V oxygen-containing compounds were studied. The E=O (E—O) groups were found to be transformed into the EF_2 (E—F) (E = Sb or Bi) groups.

Key words: hexafluoropropene oxide, substitutive fluorination, triphenylantimony difluoride, triphenylbismuth difluoride.

Earlier, we have studied the reaction of hexafluoropropene oxide (HFPO) with phosphoryl compounds.[1,2] It was shown that the P=O groups were thereby transformed into the PF_2 groups. Taking into account that this reaction occurs relatively smoothly with compounds containing a very stable phosphoryl P=O group, one could assume that such transformations are also possible in the case of compounds of other Group V elements containing the E=O group.

With the goal of testing this assumption, we introduced some oxygen-containing compounds of antimony and bismuth into reaction with HFPO. It turned out that HFPO reacts with $Ph_3Sb=O$ even at room temperature to give Ph_3SbF_2.

$$Ph_3Sb{=}O \longrightarrow Ph_3SbF_2$$

Ph_3SbF_2 was identified by ^{19}F NMR spectroscopy. The chemical shift of the Ph_3SbF_2 formed ($\delta_F(CF_3COOH)$ −75.1) corresponded to $\delta_F(CFCl_3)$ −153.2 described in the literature.[3] The product[4] of a reaction that we reproduced possessed a similar chemical shift (δ_F −75).

$$Ph_3Sb + XeF_2 \longrightarrow Ph_3SbF_2.$$

The yield of Ph_3SbF_2 was determined by integrating the signals for Ph_3SbF_2 and *m*-fluorotoluene, which was added to the reaction mixture after the reaction was

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1652—1653, August, 1998.