Oxyanions Catalyze Group-Transfer Polymerization To Give Living Polymers†

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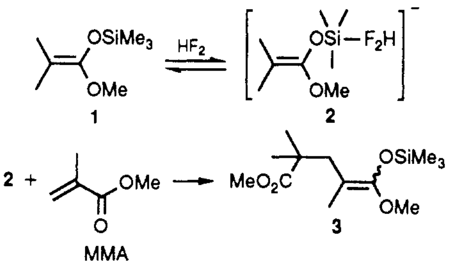
ABSTRACT: Oxyanions form a new class of catalysts for group-transfer polymerization (GTP) of acrylic monomers. Active catalysts in this class include aliphatic and aromatic carboxylates, phenolates, sulfinates, phosphinates, sulfonamidates, perfluoroalkoxides, nitrite, and cyanate. Catalytic activity is found in oxyanions whose conjugate acids have a pK_a (in DMSO) within the range 4.5–23. Best results in terms of livingness and polydispersity of the resulting polymers are obtained with the lowest operable concentrations of the most active catalysts and with somewhat higher concentrations of catalysts of moderate activity. Bioxyanions (1:1 complexes of oxyanions with their conjugate acids) also are active but show reduced activity compared to the corresponding monooxyanions. They give better control of molecular weight than is obtained with the corresponding monooxyanions. In contrast to the more potent catalysts, the weaker catalysts show little activity at temperatures substantially below room temperature. Relative catalyst efficiency correlates well with pK_a(DMSO) of the conjugate acids of the corresponding catalysts. The stereochemistry of PMMA prepared with oxyanion catalysts does not differ substantially from that of PMMA prepared with bifluoride catalysis.

Introduction

Group-transfer polymerization (GTP) gives monodisperse living (meth)acrylate polymers in which the degree of polymerization is determined by the monomer: initiator ratio.[1] The process, illustrated in Scheme I for methyl methacrylate (MMA), is catalyzed by anions such as fluoride, difluorotrimethylsiliconate, bifluoride, azide, and cyanide as tris(dimethylamino)sulfonium (TAS) or tetraalkylammonium salts. Even though selected Lewis acids also catalyze the process,[1b] the anions are preferred because they can be used at very low concentrations. However, because of their simple structure, the anionic catalysts previously reported do not provide a broad latitude in controlling GTP through variation of catalyst structure.

We now report that the scope of catalysis of GTP is exceptionally broad in that it encompasses a multitude of oxyanions. The new class of catalysts includes carboxylate, phenolate, sulfinate, phosphinate, sulfonamidate, and perfluoroalkoxide[2] ions and the corresponding bioxyanions[3] (1:1 complexes of oxyanions with their conjugate acids). Since their basicity, and consequently their catalytic activity, can be controlled, for example, through substitution, *the oxyanions allow the GTP practitioner to fine-tune the reaction conditions in order to optimize and control livingness, polydispersity, and molecular weight.* Simple inorganic oxyanions, such as nitrite and cyanate, also catalyze GTP. As reported for bifluoride,[4a] some of these oxyanions catalyze simple condensations of silyl ketene acetals with aldehydes, ketones, and Michael acceptors. After we had made our observations concerning oxyanion catalysis, Effenberger reported[5] that *tert*-butoxide and acetate catalyze the electrophilic substitution reactions of aryl and heterocyclic silanes. Our mechanistic studies have suggested that the complex, 2, formed between a bifluoride catalyst and the silyl ketene acetal is a reactive intermediate in GTP,[1c] and we presume that analogous complexes are formed in the oxyanion-catalyzed GTP.

Scheme I



Experimental Section

Materials. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl prior to use. Toluene was dried over 4-Å molecular sieves, distilled from sodium, and stored over 4-Å molecular sieves. Acetonitrile was distilled from P_2O_5 and stored over 4-Å molecular sieves. Aqueous (40%) tetrabutylammonium hydroxide (TBAOH), methanolic TBAOH (1.0 M), and the conjugate acids of the catalysts were purchased from Aldrich Chemical Co. and used without further purification. Tetrabutylammonium acetate, purchased from Fluka Chemical Corp., was used without further purification in the study presented in Table IV. Tetrabutylammonium fluoride trihydrate, tetraethylammonium cyanate, and tetrabutylammonium nitrite were purchased from Fluka Chemical Corp. and used as received. The preparation and purification of tris(dimethylamino)sulfonium bifluoride ($TASHF_2$) were described elsewhere.[1a,4] Methyl, 2-(dimethylamino)ethyl, 2-(trimethylsiloxy)ethyl, 2-ethylhexyl, and *n*-butyl methacrylates were purchased from common vendors and purified prior to use by passage through neutral alumina (Woelm, activity I) under an atmosphere of dry argon. Tetrahydropyranyl methacrylate (THPMA) was prepared according to a published procedure.[6] GTP initiators were prepared as described earlier.[1d] Molecular weights were determined by gel permeation chromatography (GPC) in THF using a Waters Associates 590 pump, a 401 refractive index detector, and four consecutive μStyragel columns (100 000, 10 000, 500, and 100 (PMMA standards)). Values of $\bar{M}_w/\bar{M}_n$ are reported as *P*. Proton NMR spectra were recorded on a Nicolet 360WB spectrometer.

Preparation of Catalysts[7] (Method A). This procedure is designed for the more acidic phenols and carboxylic acids as opposed to the less acidic phenols. To 5.0 g of the acid in a separatory funnel was added 1.5 equiv of 40% aqueous TBAOH (1.5 M). This mixture was shaken in a separatory funnel until the acid dissolved or until further dissolution ceased. The solution was then extracted three times with a volume of dichloromethane equal to that of the volume of TBAOH solution that had been used. The combined dichloromethane extracts were

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dried ($MgSO_4$), filtered, and evaporated promptly (since dichloromethane is susceptible to attack by the oxyanions). To the residue was added 100 mL of toluene, and the solvent was evaporated on a rotary evaporator to remove excess water as an azeotrope. This was done three times after which the catalyst was dried at 0.1 Torr at 25 °C for 2 days. In most cases, solids of analytical purity were obtained.[8] They are readily soluble in acetonitrile, partly soluble in chloroform, and only marginally soluble in toluene or THF. In all cases, 1.5 equiv of base was used relative to the organic acid.[9] The extraction of 4-nitrophenol, even with excess base, gave only the corresponding bioxyanion. In the latter case, the use of method B provided the desired monooxyanion.

Preparation of Catalysts (Method B). This procedure is designed for the less acidic phenols as opposed to the more acidic carboxylic acids. To a dry round-bottomed flask containing 5 g of the acid and a magnetic stirring bar was added 1.0 equiv of TBAOH (1.0 M in methanol). The acid dissolved within 60 min with stirring. The mixture was evaporated to dryness, and the residue was treated with 3 × 5 mL of dry toluene and dried at 0.1 Torr for 2 days.

General Procedure for the Preparation of Bioxyanions. The procedure is illustrated by the preparation of tetrabutylammonium bibenzoate. To 10 g of benzoic acid in a separatory funnel was added 80 mL of 40% aqueous TBAOH. The mixture was shaken until it became homogeneous and then extracted with 3 × 50 mL of dichloromethane. To the combined extracts was added 10 g of benzoic acid, and the solution was dried ($MgSO_4$), filtered, and evaporated. The residual solid was dissolved in 250 mL of warm THF, and the volume was reduced to 125 mL using an aspirator. To the partly crystallizing mixture was added 250 mL of ether (in parts), and the mixture was allowed to stand overnight. The product was filtered, washed with ether, and dried at 0.1 Torr. Anal. Calcd: C, 74.24; H, 9.67; N, 2.89. Found: C, 74.27; H, 9.88; N, 2.84. Mp 103–105 °C. The compositions of all catalysts were confirmed by ^1H NMR. Unless otherwise indicated, all catalysts had satisfactory elemental analyses.

General Procedure for Controlled Increase in $\bar{M}_n$ of Poly(methyl methacrylate) (PMMA) (Table I). To a three-necked, 100-mL, round-bottomed flask fitted with a septum, thermocouple well, and stopper, under argon, were added 30 mL of THF and 0.20 mL (1.0 mmol) of 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (1).[1d] To the stirred solution was added 0.02 mmol (2 mol % relative to 1) of the catalyst solution (0.28–0.55 M in acetonitrile). After 5 min, 5.0 mL (47.6 mmol) of MMA was added via a syringe at a rate of 1.0 mL/min. An exothermic reaction occurred. Exactly 1 h after the maximum temperature was reached, a 0.5-mL aliquot of the reaction mixture was withdrawn (A) after which 5.0 mL more of MMA was added at a rate of 1.0 mL/min. A similar, but usually slightly lower, maximum temperature accompanied the resulting exotherm. After 1 h from the time the maximum temperature was reached, a second 0.5-mL aliquot was withdrawn (B), and a third 5.0-mL portion of MMA was added at 1.0 mL/min. The third 0.5-mL aliquot (C) was withdrawn at least 1 h from the time of peak temperature. A fourth 5.0-mL portion of MMA was added (all at once) after 15 h. If no exothermic reaction occurred following this addition, an acetonitrile solution of an additional 0.01 mmol of the catalyst was added. The mixture was stirred for 2 h and the polymerization quenched with methanol. After an additional 2 h of stirring, the polymer was precipitated in hexane, collected by filtration, and dried at 80 °C/20 Torr, and a final polymer sample (D) was removed for GPC analysis. The polymer samples A, B, and C were similarly isolated and then analyzed by GPC.

General Procedure for Preparation of PMMA with $\bar{M}_n$ up to 60 000 (Table IV). A 500-mL, four-necked flask was fitted with a magnetic stirring bar, an argon inlet adapter, a thermocouple, a rubber septum, and a 125-mL pressure-equalizing dropping funnel. The apparatus was dried at 160 °C and assembled while hot (heat gun) under an argon flush. Dry THF (225 mL) was transferred via cannula to the reaction flask, and the dropping funnel was charged with 75 mL (694 mmol) of MMA. The funnel was capped with a rubber septum, and the ungreased joints were sealed with Parafilm. To the stirred solution, under argon, was added 0.37 mL (1.2 mmol) of 1-(2-(trimethylsiloxy)ethoxy)-1-(trimethylsiloxy)-2-methyl-1-propene (3)[1d] followed by 50 μL of tetrabutylammonium biacetate (0.04 M, 0.002 mmol) in THF.[10] MMA was then added over a 120-min period, and the temperature rose steadily from 24 to 35 °C. The solution remained fluid throughout the addition of monomer but viscosity increased steadily as polymerization proceeded afterward. The solution was stirred for 5 h after completion of the monomer addition and was left unstirred for another 16 h, whereupon it was quenched with 10 mL of methanol. After 1 h, the solution was poured very slowly into a 5-fold volume of hexane agitated strongly in a blender. After filtration and washing with hexane, the polymer was dried to constant weight in a vacuum oven at 65 °C under a slow nitrogen purge. Conversion was 100% of theory. $\bar{M}_n$(theory) = 60 000. GPC: $\bar{M}_n$ = 57 900, $\bar{M}_w$ = 65 700, P = 1.13.

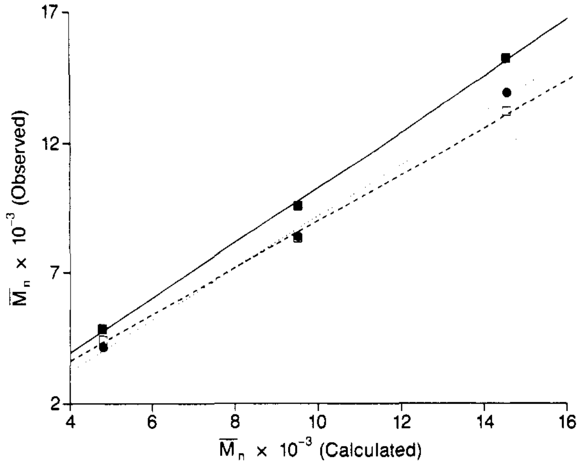


Figure 1. Molecular weight control in GTP [$\bar{M}_n$(obsd) vs $\bar{M}_n$(calcd)] with the catalysts tetrabutylammonium 4-(methylsulfonyl)benzoate (●), 4-nitrobenzoate (■), and biacetate (□).

Catalysis of GTP of MMA with Tetraethylammonium Cyanate. To a 25-mL THF solution of 20 μL of tetraethylammonium cyanate (1 M in acetonitrile) was begun the addition of 10 g (100 mmol) of MMA. After 3 mL of the monomer was added, the addition was interrupted for 1 h after which time an aliquot of the reaction mixture was removed and found to contain no polymer. Then 0.87 g (1.0 mL, 5 mmol) of 1 was added with a concomitant rise in temperature. Dropwise addition of the remaining monomer was resumed. After 1 h an aliquot was removed for GPC analysis which gave $\bar{M}_n$ = 2690, $\bar{M}_w$ = 3240, and P = 1.20 [$\bar{M}_n$(theory) = 2100]. An additional 5 g of MMA was then added, giving an exothermic reaction. Removal of solvent gave a quantitative yield of PMMA. $\bar{M}_n$(theory) = 3100. GPC: $\bar{M}_n$ = 4130, $\bar{M}_w$ = 5360, P = 1.30.

Results and Discussion

Scope of Catalysis. As in the case of the previously reported GTP catalysts, the oxyanions mentioned above give living polymers of low polydispersity whose molecular weights are controlled by the ratio of monomer to initiator. This is illustrated by the correspondence between $\bar{M}_n$(obsd) and $\bar{M}_n$(calcd) as depicted in Figure 1.

To examine molecular weight control and polydispersity under oxyanion catalysis, a standardized polymerization procedure in which monomer was polymerized by interrupted additions was developed. The first monomer addition was designed to give $\bar{M}_n$ = 4800. After a period of 1 h from the time maximum temperature (T_{max}) was reached, a second batch of monomer, sufficient to double the $\bar{M}_n$ to 9500, was added. A second waiting period was followed by addition of more monomer to bring the $\bar{M}_n$ to 14 500. After 15 h, additional monomer was added to give a final $\bar{M}_n$ of 19 300. By withdrawing samples for GPC analysis after each addition of monomer, a molecular weight history of the polymer was obtained that revealed the extent to which the polymer was living and $\bar{M}_n$ was increasing. The results are summarized in Table

Table I
Catalysis of GTP of Methyl Methacrylate by Oxyanions Using Sequential Monomer Feeds[a]

entry	cat. (prep. method)[b]	pK_a(DMSO)	% yield[c] in feeds A/B/C/D	$\bar{M}_n$(A)/P[d] (obsd)
1	2-nitrobenzoate[h] (A)	8.1	q/q/0/-	
2	4-nitrobenzoate (A)	9.0[m]	q/q/q/0	4470/1.51
3	4-cyanobenzoate (A)	9.1[m]	q/q/q/0	4080/1.49
4	3-nitrobenzoate (A)	9.2	q/q/q/83	3370/1.43
5	4-(methylsulfonyl)benzoate (A)	9.4[m]	q/q/q/46	4170/1.24
6	4-(trifluoromethyl)benzoate·H_2O (A)	9.8[m]	q/q/q/q	4410/1.10
7	3-chlorobenzoate (A)	9.9[m]	q/q/q/q	4340/1.18
8	4-chlorobenzoate·H_2O (A)	10.1	q/q/q/q	4660/1.61
9	benzoate (A)	10.5	q/q/q/0	4500/1.38
10	4-methoxybenzoate[f,g] (A)	11[m]	q/q/q/0	4830/1.27
11	cyanoacetate[f] (B)	6.2[m]	50/-/-/-	6160/1.55
12	acrylate[f] (A)	11[m]	q/q/q/0	4710/1.29
13	biacetate·0.2HOAc[e]	11.5	q/q/q/0	4450/1.28
14	picolinate[f] (A)	12.8	q/q/q/72	4350/1.50
15	pentachlorophenolate (B)	7.05	37/-/-/-	3470/1.43
16	pentafluorophenolate (A)	7.5	q/q/q/0	4210/1.25
17	2,4,6-trichlorophenolate (B)	10.2	q/q/q/28	4420/1.36
18	2-nitrophenolate (B)	10.8[m]	q/q/q/0	6410/1.14
19	4-nitrophenolate·1.4H_2O (B)	11[m]	q/q/q/q	4930/1.16
20	4-cyanophenolate (B)	13.1	q/q/0/-	4940/1.09
21	3-nitrophenolate·1.7H_2O (B)	13.4	q/q/q/q	4860/1.06
22	4-fluorophenolate[i] (B)	17.1[m]	q/q/92/0	5190/1.10
23	4-methoxyphenolate[l] (B)	17.8[m]	q/q/42/0	5350/1.11
24	*N*-methyl-*p*-toluenesulfonamide·0.5H_2O (B)	*k*	q/q/q/0	4510/1.07
25	phenylphosphinate·H_2O (B)	*k*	q/q/q/17	5300/1.11
26	4-methylbenzenesulfinate (A)	~4.5[m]	q/q/q/0	*k*
27	4-methylbenzenesulfinate[j] (A)	~4.5[m]	q/q/0/-	4370/1.24
28	nitrite	*k*	q/q/q/24	6320/1.35

[a] $\bar{M}_n$(theor) based on monomer charged: A = 4800, B = 9500, C = 14 500, D = 19 300. All catalysts are tetrabutylammonium salts dissolved in acetonitrile used at 2 mol % of initiator. Solvent is THF. [b] For details of methods A and B, see Experimental Section. [c] q = quantitative yield. [d] P = polydispersity. [e] Made by neutralizing tetrabutylammonium hydroxide with excess acetic acid and triturating the product with ether. [f] Satisfactory elemental analysis not obtained. [g] Used 0.01 mmol of catalyst (one-half of normal). [h] Second aliquot monomer added after 1 day; third added after 3 more days. [i] GPC sample withdrawn 16 h after the prior monomer addition. [j] Run in DMF instead of THF; third aliquot of MMA added the next day. [k] Not determined. [l] No elemental analysis. [m] Calculated based on ref 13.

Table II
Relationship between the Conjugate Acidities of the Oxyanion Catalysts, Δt_{max}, and ξ_r

oxyanion[a]	pK_a(DMSO)[12,13]	Δt_{max}	ξ_r	oxyanions[a]	pK_a(DMSO)[12,13]	Δt_{max}	ξ_r
benzoates				phenoxides			
3,5-DNB[b]	7.4	*c, f*		$C_6Cl_5O^-$	7.05	*c*	
salicylate	6.8	8.0	0.70	$C_6F_5O^-$	7.5[d]	29	0.19
2-NO_2-B	8.1	120	0.05	2,4,6-Cl_3PhO^-	10.2	11	0.51
4-NO_2-B	9.0[d]	12	0.47	bi-4-NO_2PhO^-	11[d,e]	11	0.51
3-NO_2-B	9.2	32	0.18	2-NO_2PhO^-	10.8[d]	6.5	0.86
4-CN-B	9.1[d]	13	0.43	4-$CNPhO^-$	13.1	5.1	1.10
4-CH_3SO_2-B	9.4[d]	11	0.51	3-NO_2PhO^-	13.4	4.7	1.19
4-CF_3-B	9.8[d]	27	0.21	4-$FPhO^-$	17.1[d]	5.0	1.12
3-Cl-B	9.9[d]	6.1	0.92	bi-PhO^-	18[d,e]	5.1	1.10
bi-3-Cl-B	~9.9[d,e]	21	0.27	4-$MeOPhO^-$	17.8[d]	5.5	1.02
4-Cl-B	10.1	13	0.43	misc anions			
benzoate	10.5	5.6	1.00	4-$MePhSO_2\tilde{N}Me$	*g*	5.5	1.02
bibenzoate	~10[d,e]	6.0	0.93	$PhPH(O)O^-$	*g*	5.4	0.04
4-MeO-B	11[d]	4.7	1.19	4-$MePhSO_2^-$	~4–5[d]	~12	0.47
aliphatic carboxylates				NO_2^-	*g*	6.2	0.90
$CF_3CO_2^-$	1.3[d]	*c, f*		*p*-$MePhSO_3^-$	*g*	*c, f*	
$Me_32NCH_2CO_2$	5.9[d]	*c, f*					
$NCCH_2CO^-$	6.2[d]	*c*					
OAc/bi-OAc	11.5	5.0	1.12				
acrylate	11[d]	4.3	1.30				

[a] Cation = tetrabutylammonium. [b] B = benzoate. [c] No exotherm. [d] Calculated based on ref 13. [e] Assumed to be close to the parent acid. [f] No monomer conversion; not a catalyst under these conditions. [g] Unknown.

I. Only in the last monomer addition do differences among the catalysts become apparent in that certain catalysts produced little or no polymers. As will be discussed, all catalysts can be induced to give longer lived polymerizations by decreasing the concentration of catalyst.

A general conclusion that can be drawn from the data is that although there are differences among the catalysts with respect to control of molecular weight and monomer conversion particularly in the final monomer feed, these differences are minor and the observed molecular weights increase in a linear fashion with monomer consumption. With regard to livingness as judged by yields of all feeds, the benzoates, as a class, gave the most satisfactory results. The studies show that the least basic benzoates [pK_a(DMSO) = 7–9] do not give as good a result as do those derived from acids with pK_a(DMSO) = 10.5 ± 0.6. Among the aliphatic carboxylates (entries 11–13) acetate and acrylate gave somewhat acceptable results whereas the nonbasic cyanoacetate gave poor conversion and molecular weight control. With respect to polydispersity, phenolates (entries 14–23) gave polymers of the narrowest molecular weight distribution. The phenolates, as a class of oxyanion catalysts, gave less "living" polymers (compared to benzoates) as judged by the incomplete conversions obtained in the third and fourth feeds even though the monosubstituted ones (entries 18–23) gave dispersities of 1.06–1.11 for the first feed. In general, highly basic oxyanions [pK_a(DMSO) > 13] tend to give less living polymers. The last class (entries 24–28) of catalysts are weakly basic [calculated pK_a(DMSO) ~ 4.5] and are expected to give very slow polymerizations. Thus, 4-methylbenzenesulfinate gave slow polymerizations in THF (entry 26) but was faster in the more polar solvent, DMF (entry 27), with satisfactory results.

The catalysts studied in Table I are all tetrabutylammonium salts. In general, noncoordinating cations, such as TAS and tetraalkylammonium cations, give the most satisfactory results, whereas alkali-metal carboxylates, such as sodium acetate, give less satisfactory results.

Catalyst Activity. In order to qualitatively assess catalyst effectiveness in the absence of actual rate data, an arbitrary standardized reaction protocol was established based on the first addition of the polymerizations described in Table I. The exothermic polymerizations produced an increase in temperature as monomer was consumed, reaching a maximum, T_{max}, after the monomer addition (5 min) was completed. The length of time elapsed from the beginning of the monomer feed until T_{max} was reached, defined as Δt_{max}, depended critically upon the identity of the catalyst (typically, Δt_{max} values were reproducible to within ±10%).

There appears to be a correspondence between the valus of Δt_{max} (see Table II) and the nonaqueous acidities of the conjugate acids of the catalysts measured[12] or calculated[13] in DMSO. Though there are exceptions, the catalysts derived from the weakest acids (most basic oxyanions) give the shortest Δt_{max}, whereas catalysts derived from the strongest acids (least basic oxyanions) give the longest Δt_{max}. The conversions of monomer at T_{max} for fast catalysts (short Δt_{max}) were the same (>90%) within experimental error (data not shown). However, in the case of slower catalysts (long Δt_{max}), the conversions at T_{max} varied depending upon the type of catalyst. Hence, qualitatively, Δt_{max} tracks conversion. This provides a very fast assay for assessing the efficiencies of the various catalysts.[14a]

In order to get a qualitative insight into the relationship between catalyst efficiency and basicity and provide some guidance in selecting an oxyanion as a GTP catalyst, we define catalyst efficiency, ξ, as the moles of monomer consumed per mole of catalyst per unit time. Thus

$$\xi_i = M_T/\{m_i(\Delta t_{max})_i\} \tag{1}$$

where M_T is the total moles of monomer consumed and m_i is the moles of catalyst i. A relative efficiency, ξ_r, is, therefore, defined as

$$\xi_r = \xi_i/\xi_j = \{(M_T)_i m_j (\Delta t_{max})_j\}/\{(M_T)_j m_i (\Delta t_{max})_i\} \tag{2}$$

where m_j is moles of reference catalyst j. If concentrations of catalysts are kept constant and the amount of polymer to be produced is fixed, then the unitless quantity ξ_r is reduced to

$$\xi_r = (\Delta t_{max})_j/(\Delta t_{max})_i \tag{3}$$

Hence if one knows the time it takes to produce a given amount of polymer under a defined set of conditions, one should be able to estimate ξ_r. In our studies the relative efficiency, ξ_r, for each catalyst was determined relative to benzoate[14b] whose rate order has been independently determined by kinetic measurements to be unity.[15]

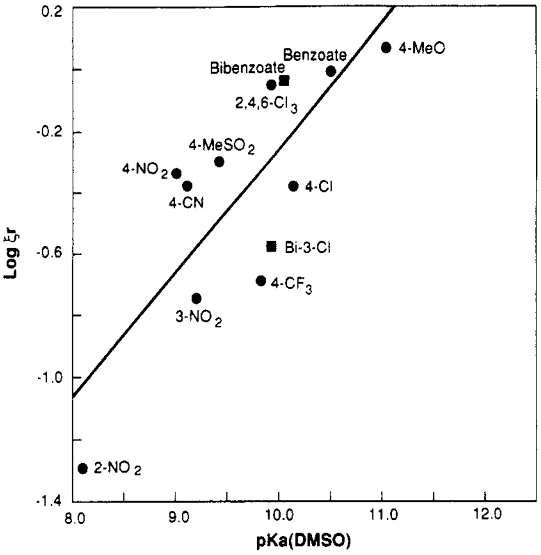


Figure 2. Correlation of pK_a(DMSO) of conjugate acid of benzoate catalysts and apparent relative catalyst efficiencies for GTP of MMA.

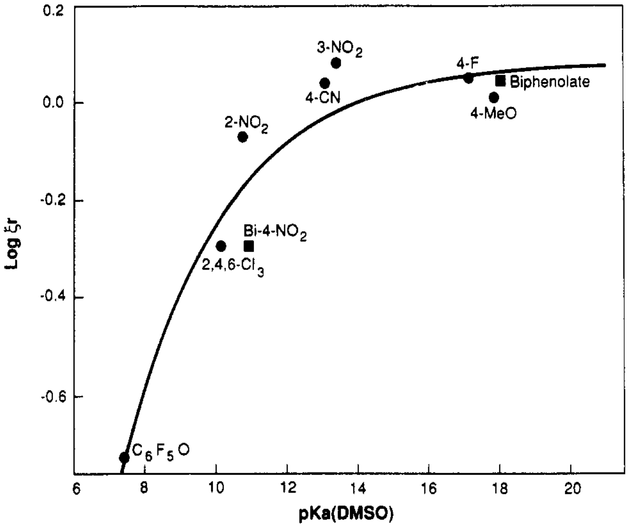


Figure 3. Correlation of pK_a(DMSO) of conjugate acid of phenolate catalysts and apparent relative catalyst efficiencies for GTP of MMA.

Table III
Bioxyanion-Catalyzed GTP

entry	cat.[a]	monomer	$\bar{M}_n$(calcd)	$\bar{M}_n$(obsd)	$\bar{M}_w/\bar{M}_n$
1	biacetate	MMA	4780	4450	1.28
2	biacetate	MMA	60000	57900	1.13
3	biacetate	BMA	5840	5140	1.10
4	biacetate	BMA	56900	67600	1.13
5	biacetate	EHMA	56000	41600	1.30
6	bibenzoate	DMAEM[b]	9400	8250	1.07
7	bibenzoate	TMS–HEMA[c]	4760	4750	1.41
8	bibenzoate	THPMA[d]	4760	4120	1.10
9	bibenzoate	THPMA, MMA[e]	8600	7730	1.08
10	biacetate	DMAEM, MMA[e]	9440	8690	1.07

[a] Cation = tetra-*n*-butylammonium. [b] (Dimethylamino)ethyl methacrylate. [c] 2-(Trimethylsiloxy)ethyl methacrylate. [d] Tetrahydropyranyl methacrylate.[6] [e] Block opolymer.

The values of ξ_r for the various catalysts are listed in Table II. Figures 2 and 3 show plots of log ξ_r vs pK_a(DMSO) of the conjugate acids of the catalysts,[14c] where

Table IV
GTP Catalysis with Bioxyanions and Monooxyanions Using Sequential MMA Additions

entry	cat.	% yield^a A/B/C/D	$\bar{M}_n$(A)/P^b	$\bar{M}_n$(B)/P	$\bar{M}_w$(C)/P	$\bar{M}_n$(D)/P
1	benzoate	q/q/q/0	4500/1.38	10500/1.4	15200/1.81	15900/1.56
2	bibenzoate	q/q/q/0	4680/1.06	8170/1.12	14200/1.16	13900/1.23
3	3-chlorobenzoate	q/q/q/q	4340/1.18	8960/1.11	13600/1.17	17600/1.35
4	bi(3-chlorobenzoate)	q/q/q/q	4650/1.03	9030/1.05	14000/1.09	19000/1.18
5	4-nitrophenolate	q/q/q/0	4930/1.16	9360/1.28	14900/1.34	ND^c
6	bi(4-nitrophenolate)^d	q/q/q/q	4850/1.04	9610/1.06	15200/1.12	18900/1.39

^{a} q = quantitative yield. A, B, C, and D are the interrupted additions. ^{b} $P = \bar{M}_w/\bar{M}_n$. ^{c} ND = not determined. ^{d} Prepared by method A.

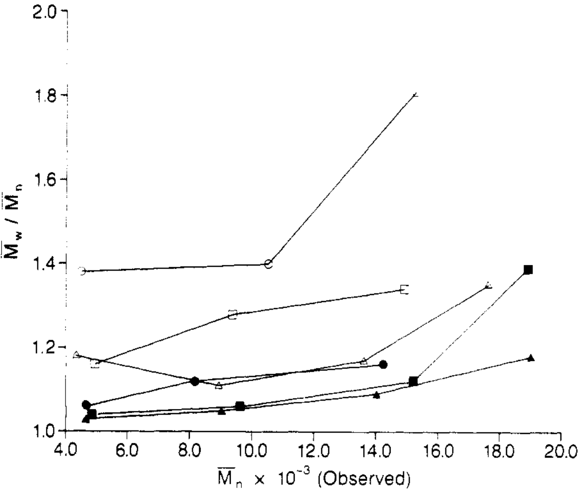


Figure 4. Comparison of effects on polydispersity ($\bar{M}_w/\bar{M}_n$) of PMMA with catalysis by the oxyanions and the bioxyanions tetrabutylammonium benzoate (○), bibenzoate (●), 3-chlorobenzoate (△), bi(3-chlorobenzoate) (▲), 4-nitrophenolate (□), and bi-(4-nitrophenolate) (■).

$$\log(\xi_r)_i = \log\frac{(\Delta t_{\max})_{\text{benzoate}}}{(\Delta t_{\max})_i} \tag{4}$$

The plot of Figure 2 suggests that, for benzoates, the relative catalyst efficiency, ξ_r, correlates somewhat with pK_a(DMSO) of the conjugate acids. However, for phenolates (Figure 3), it appears that at pK_a(DMSO) ≥ 13.8 the relative efficiency, ξ_r, is invariant regardless of the type of catalyst. For the sake of comparison and completeness, selected bianions are shown (as filled squares) on the plots of Figures 2 and 3 even though their mode of operation is not clearly understood. This apparent constant region of the plot (i.e., pK_a(DMSO) ≥ 13.8) is very likely a result of the inability of our method to adequately measure ξ_r for very fast catalysts. To determine if the shape of the curve reflects a change in mechanism, detailed kinetic measurements, preferably with a stopped-flow apparatus, will have to be done (in progress). If the results hold, it may suggest that for oxyanion catalysts with conjugate acid pK_a(DMSO) ≥ 13.8, a common species is produced which then serves as the catalyst. Alternatively, it could reflect a change in mechanism, for example, from an associative to a dissociative one.[1c] The paucity of appropriate kinetic data makes any detailed interpretation of the plot of Figure 3 purely speculative at this point. However, it is important to point out that despite the qualitative nature of the above correlations, the method provides the appropriate guidance for the selection of an operable GTP catalyst.

Bioxyanions and Effect of Catalyst Concentration on GTP. Because of their ease of preparation, crystallinity, nonhygroscopic nature, and uniformly good polymerization results with a variety of monomers, the bioxyanions were judged to be superior catalysts (see Table III). Catalysis proceeds with somewhat better molecular weight control than is obtained with the corresponding monooxyanions. Low polydispersity was obtained at both high $\bar{M}_n$ (Table III, entries 2, 4, and 5) and low $\bar{M}_n$ (Table III, entries 1, 3, and 6–8). Low polydispersities were also obtained with block copolymers (Table III, entries 9 and 10). For successive buildup of molecular weight using the same

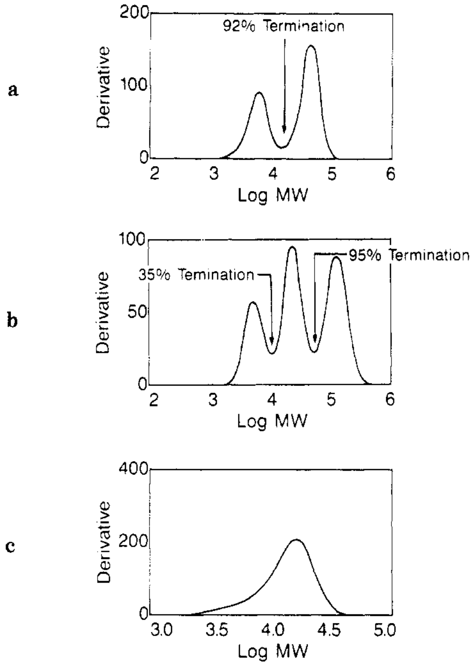
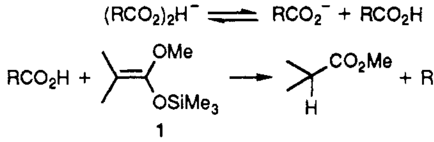


Figure 5. GPC traces of PMMA prepared with various levels (expressed as mole percent of initiator) of tetrabutylammonium benzoate catalyst, using three sequential additions of MMA: (a) 2.2%, M_p = 5210 and 40 400; (b) 0.55%, M_p = 4540, 20 100, and 108 000; (c) 0.14%, M_p = 12 000 (sh 4000) (M_p = peak molecular weight).

Scheme II



Scheme III

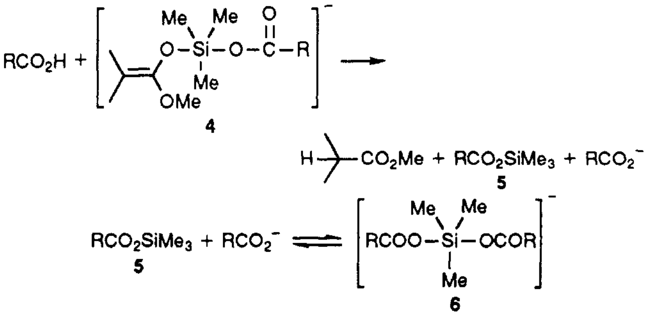


Table V
Effect of Catalyst Concentration on Polymerization of MMA[a]

entry	cat.[b]	([cat.]/[init]) × 100	conv,[c] %	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$(GPC)	$\bar{M}_n$(theor)[d]
1	TBAF·3H$_2$O	0.70	9	4.33	13 900	60 000
2	TBAF·3H$_2$O	0.034	100	1.14	64 700	60 000
3	TBA biacetate	21.5	*e*	*e*	*e*	60 000
4	TBA biacetate	1.7	100	1.48	68 900	60 000
5	TBA biacetate	0.34	97	1.15	56 000	56 000
6	TBA acetate	0.69	35	4.57	27 600	60 000
7	TBA acetate	0.07	100	1.09	55 500	60 000

[a] Polymerization in dry THF (225 mL) at autogenous temperature (initial 25 °C, peak 32–38 °C) with 1-(2-(trimethylsiloxy)ethoxy)-1-(trimethylsiloxy)-2-methyl-2-propene (TTEB, 0.37 mL) and MMA (75 mL, fed in at 0.7–1.0 mL/min). [b] Catalyst solution: 0.02 M n-Bu$_4$NF·3H$_2$O/THF, 0.5 M n-Bu$_4$NOAc·HOAc/CH$_3$CN, and 0.04 M n-Bu$_4$NOAc/THF. [c] Calculated from the weight of isolated polymer. [d] Calculated from the monomer:initiator molar ratio. [e] Incomplete polymerization.

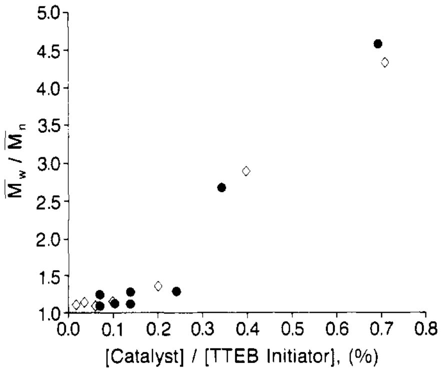


Figure 6. Correlation of mole percent of catalyst relative to initiator (TTEB) and polydispersity ($\bar{M}_w/\bar{M}_n$) in GTP of PMMA catalyzed by tetrabutylammonium acetate (●) and fluoride (◇).

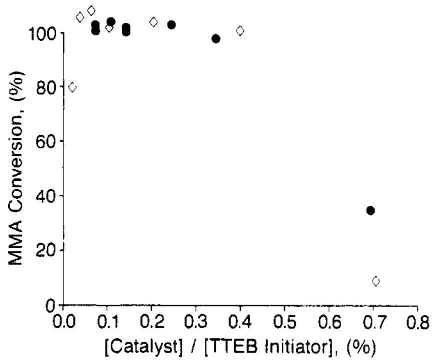


Figure 7. Correlation of mole percent of catalyst relative to initiator (TTEB) and MMA conversion in GTP of MMA catalyzed by tetrabutylammonium acetate (●) and fluoride (◇).

general procedure described for the controlled increase in $\bar{M}_n$ of PMMA (Table I), the bi-salts of benzoate (Table IV, entry 2), 3-chlorobenzoate (Table IV, entry 4), and 4-nitrophenolate (Table IV, entry 6) provided more monodisperse PMMA than the corresponding monooxyanions (Table IV, entries 1, 3, and 5). These results are shown graphically in Figure 4. The reason for this improvement is not fully understood but it closely parallels the improvement previously reported[1a] for bifluoride relative to difluorotrimethylsiliconate (which serves as a source of highly reactive fluoride oxyanion).

A plausible explanation for the improved catalytic behavior of bioxyanions is that they are serving as a source of low concentrations of monooxyanions via the dissociation equilibrium shown in Scheme II. However, it is unlikely that the equivalent of carboxylic acid that forms will survive in the presence of the silyl ketene acetal, the living polymer, or their corresponding activated complexes (analogous to **4** in Scheme III). Instead, the carboxylic acid will react with either the initiator (as shown in Scheme II), the living polymer, or their activated complexes (Scheme III) to give an inert methyl isobutyrate or dead (protonated) polymer and trimethylsilyl carboxylate (**5**) as byproducts. The silyl ester may then form a complex (**6**) with the monooxyanion via the equilibrium shown in Scheme III. Depending upon the affinity of the particular oxyanion for silicon, the concentration of the monooxyanion will be maintained at a low but an effective level throughout the course of the reaction. Since total catalyst concentration is low, the loss of initiator or living end in Schemes II and III will have an undetectable effect on molecular weight and polydispersity. Such a mechanism is plausible, giving the observed slowing in reaction rate and increased livingness associated with the external addition of silyl esters, **5**.[16]

That lower concentrations of a carboxylate will give better results is demonstrated by the fact that with successive reductions in the concentration of the tetrabutylammonium benzoate, molecular weight control, polydispersity, and conversion are improved. This is illustrated in Figure 5 for PMMA made by a polymerization procedure using three successive monomer additions. With a catalyst level (relative to initiator) of 2.2 mol %, the molecular weight distribution is bimodal and only the first two batches of monomer are consumed. Analysis of the molecular weight distribution (Figure 5a) indicates that 92% of the chain ends are terminated prior to the start of the second monomer addition. When the catalyst concentration is reduced fourfold to 0.55% of the initiator, the third batch of monomer is completely consumed. However, due to occurrence of substantial chain termination between additions (35% before the start of the second addition, a total of 95% before the start of the third addition), the molecular weight distribution of the isolated polymer is trimodal (Figure 5b). With the catalyst concentration further reduced to 0.14% of initiator, all three batches of monomer are polymerized with good molecular weight control, and the molecular weight distribution is unimodal. However, the GPC trace in this case tails slightly in the low molecular weight region (Figure 5c), suggesting some chain termination.

The beneficial effect of reducing the catalyst:initiator ratio is especially pronounced in higher molecular weight polymers. For tetrabutylammonium fluoride trihydrate (Table V, entries 1 and 2), biacetate (Table V, entries 3–5), and acetate (Table V, entries 6 and 7), lowered catalyst:initiator ratios lead to higher monomer conversions, lower polydispersity, and improved molecular weight control. For fluoride trihydrate and acetate catalysis, decreasing catalyst levels lead to a systematic improvement in the polydispersity (Figure 6) and conversion (Figure 7) of 60 000 molecular weight PMMA. The use of <0.3 mol % tetrabutylammonium acetate or tetrabutylammonium fluoride trihydrate gives complete conversions and the lowest polydispersities. Polymerizations with either catalyst proceed smoothly with as little as 0.034 mol % catalyst relative to

Table VI
Effect of Temperature on Tacticity of PMMA Made by Oxyanion-Catalyzed GTP

cat.	temp, °C	yield, %	$\bar{M}_n$ obsd	$\bar{M}_n$ theor	$\bar{M}_w/\bar{M}_n$	triads, % mm	triads, % mr	triads, % rr	P(m/r)	P(r/m)	diads, % sum	diads, % m	diads, % r
TAS acetate	69	66	4860	4500	1.30	7	42	51	0.75	0.29	1.04	28	72
	40	74	5270	4933	1.09	6	40	54	0.76	0.27	1.04	26	74
	−9.5	100	6600	6760	1.09	4	35	61	0.81	0.22	1.03	22	78
	−40	100	5980	6760	1.03	2	29	69	0.87	0.17	1.05	17	83
TBA acetate	68	84	5450	5680	1.20	6	41	53	0.77	0.27	1.05	27	73
	40	95	6770	5800	1.10	5	39	56	0.79	0.25	1.04	25	75
	10	100	6670	6760	1.07	5	36	59	0.78	0.23	1.01	23	77
	−9	100	6460	6760	1.04	3	35	62	0.85	0.22	1.07	21	79
TBA 3-chlorobenzoate	70	100	9270	1010	1.13	6	42	52	0.77	0.28	1.06	27	73
	40	100	1010	1010	1.13	6	41	53	0.77	0.27	1.05	27	73
	20	100	9320	1010	1.22	5	37	58	0.78	0.24	1.02	24	76
	0	43	5660	4400	1.29	4	27	59	0.82	0.23	1.06	23	77
TBA 2,4,6-trichlorophenoxide	71	100	1010	1000	1.37	6	40	54	0.75	0.27	1.02	27	73
	40	98	1040	9900	1.35	6	40	54	0.76	0.27	1.04	26	74
	9.8	35	6010	3600	1.37	4	38	58	0.82	0.24	1.07	23	77

initiator. It is interesting to note that the polydispersity–conversion–concentration curves for the two catalysts are superimposable. In their studies on GTP, Bandermann and Speikamp[11] reported a related decrease in $\bar{M}_n$ for higher molecular weight PMMA (due to incomplete conversion) which, however, appeared at a considerably higher catalyst:initiator ratio (30 mol %) than was used in this study.

In considering factors that are likely to affect the catalytic properties of bioxyanions, it should be noted that it is possible that the hydrogen-bonded complex may have a reduced nucleophilicity as a result of possible delocalization of the negative charge over more atoms than is possible for the corresponding monooxyanion. The reduced nucleophilicity of the catalyst may impart milder reactivity or "silicophilicity" (i.e., ability to interact with Si) onto the catalyst. In such cases, the resulting active complexes (analogous to 4) will have lower reactivities. This could lead to fewer side reactions and produce longer lived polymers. This effect is experimentally indistinguishable from the beneficial effect of using lower catalyst concentrations discussed above since both effects operate in the same direction. However, recognizing that the "silicophilicity" of the catalyst could be equally reduced by substituting an electron-withdrawing group into the catalyst, we have successfully moderated catalyst reactivity and obtained improved results with respect to molecular weight distribution and control by using appropriately substituted benzoates (e.g., Table I, entries 3–8) and phenolates (Table I, entries 18–23).

The results reported in this section clearly demonstrate that for polymers of well-controlled molecular weight and low polydispersity to be made using oxyanion-catalyzed GTP, one must judiciously balance catalyst "silicophilicity" and concentration. The level of catalyst that should be used appears to be the minimum that is necessary in order to achieve a desired polymerization rate. For the strong catalysts, such as fluoride trihydrate and biacetate described above, levels of <0.3 mol % gave the best results. For weaker catalysts, larger amounts may be used without deleterious effects. Mechanistically, the interplay between all of the above factors is not completely understood at the present time and further investigations are needed.

Temperature. The main operational difference between the oxyanion catalysts and the previously reported catalysts, such as bifluoride, is a difference in the rate of polymerization. At low temperatures (−78 °C) bifluoride efficiently catalyzes the GTP of MMA. In contrast, only the most basic oxyanions, such as acetate, will efficiently polymerize MMA at −78 °C. Overall, there appears to be a lower temperature limit for catalytic activity. For example, certain very nonbasic oxyanions such as pentachlorophenolate are too weak to catalyze GTP at an appreciable rate (ξ_r = 0.19, Table II) at room temperature, though they are active catalysts at elevated temperatures. Below a conjugate acid pK_a(DMSO) of ca. 4.5, little or no catalytic activity has been observed at all temperatures. For example, tetrabutylammonium trifluoroacetate and tris(dimethylamino)sulfonium *p*-toluenesulfonate do not significantly catalyze GTP, even in refluxing toluene.

Stereochemistry. The diad and triad compositional variation with polymerization temperature in PMMA prepared by GTP with TASHF$_2$ catalyst has been described,[1d] and activation parameter differences between m and r diad formation were reported as $\Delta\Delta H^{\ddagger}$ = 1.0 kcal/mol, $\Delta\Delta S^{\ddagger}$ = 1.1 eu, and $\Delta\Delta G^{\ddagger}_{273}$ = 0.7 kcal/mol. Using the same isothermal polymerization technique, we have measured the triad composition of PMMA prepared by GTP in tetrahydrofuran solution using the catalysts tris(dimethylamino)sulfonium acetate, tetrabutylammonium acetate, 3-chlorobenzoate, and 2,4,6-trichlorophenolate (see Table VI). As was reported for TASHF$_2$ catalysis, nearly Bernoullian statistics are obtained for each case since the sum of the probabilities of an m diad following an r diad and an r diad following an m diad approximate unity. The variation of the triad compositions with temperature shows that with these catalysts (as was observed with bifluoride), the syndiotactic component decreases with increasing temperature. The temperature–tacticity composition profiles of PMMA prepared with these oxyanion catalysts are similar to that of PMMA prepared with TASHF$_2$.

Conclusions

Oxyanions form a new class of catalysts for group-transfer polymerization. The results of our studies on these oxyanions provide us with the ability to relate catalytic activity to basicity and allow us to fine-tune the reaction conditions in order to control polymer characteristics. By a careful choice of catalyst, we have been able to perform GTP over a wide temperature range. The livingness of the polymers is controlled by the reaction temperature and the catalyst structure and concentration.

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(8) In certain cases, it was necessary to reheat the sample under vacuum (100 °C/0.1 Torr) in order to obtain analytically pure materials. In other cases, determination of purity by ^{1}H NMR was adequate, and further purification had no discernible effect on the polymerization results. Under the conditions of use, no degradation of the salts was noted.

(9) The expectation was that this would ensure complete conversion to the oxyanion and avoid the extraction of un-ionized acid into the CH_2Cl_2 layer. Some exceptions were encountered, such as the inability to obtain pure tetrabutylammonium acetate without contamination by acetic acid. In such cases, the actual catalyst used was a mixture of acetate and biacetate.

(10) Since tetrabutylammonium biacetate is only partially soluble in THF, a small amount of water (6 mol per mol of biacetate) was added to facilitate dissolution during the preparation of the stock solution. We do not recommend using larger amounts of this catalyst solution than reported here. The actual amount of water present in the reaction was 0.012 mmol, corresponding to 1 mol % of the initiator used. If this water reacted with the initiator, a corresponding amount of the latter (1 mol %) would be destroyed. This would lead to only a slight increase in molecular weight, which would not be detectable by GPC.

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(14) (a) We elected to use the method of measuring the exothermicity of the reaction to assess qualitatively catalyst effectiveness because it is fast and does not require the use of sophisticated microcalorimetry. Quantitative kinetic studies are in progress. (b) In an independent study, Brittain[15] found that the rate order for benzoate is unity while bibenzoate shows a fractional rate order. The choice of benzoate as the reference catalyst was purely arbitrary. Any other catalyst could have been used and the general conclusions will remain qualitatively the same, except that the plot of log ξ_r vs pK_a will give a line parallel to that of Figure 2 while the curve of Figure 3 will be translated linearly along the vertical axis. (c) The points in Figure 2 are experimentally determined where the line is computer-generated to fit the equation $\log \xi_r = m \cdot pK_a + c$, with $m = 0.40$ and $c = -4.3$. For phenolates (Figure 3), ξ_r changes exponentially as a function of pK_a(DMSO) and the equation that fits the computer-generated curve of Figure 3 is of the form

$$\log \xi_r = a - be^{-cx}$$

with $a = 0.08$, $b = 11.9$, $c = 0.36$, and $x = pK_a(\text{DMSO})$. The value of $\log \xi_r = a = 0.08$ (asymptote) gives a limiting value of $\xi_r = 1.2$, corresponding to $pK_a(\text{DMSO}) \sim 13.8$.

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