

METHANESULFONIC ACID AS A CATALYST IN THE ESTERIFICATION OF PHTHALIC ANHYDRIDE

Methanesulfonic acid (MSA) has several advantages over both para-toluenesulfonic acid (pTSA) and sulfuric acid (H_2SO_4) in its use as an esterification catalyst. The data in Table I, which were developed in the Product Applications Laboratory of ATOFINA Chemicals, Inc. Thio and Fine Chemicals, demonstrate these advantages in the preparation of di-(2-ethylhexyl) phthalate (dioctyl phthalate).

The experimental conditions were as follows: MSA was used as the commercial 70% solution, the pTSA used was commercial 95% semi-crystalline solid, and H_2SO_4 was used as a 95% solution. A 4.5% molar excess of 2-ethylhexanol was used. The reactions were set up for reflux through a Dean-Stark trap using a slow nitrogen sparge and mechanical stirring. Toluene was used as a water-azeotroping solvent. The reaction was monitored at 15-minute intervals by measuring the amount of water produced. The reaction mixture was purified by neutralization with 10% NaHCO_3 solution, water washing, steam distillation and a final vacuum stripping to remove excess alcohol and residual toluene.

Several runs were completed for each set of conditions, and the averaged results are presented in Table I. As can be seen in Table I, the ultimate conversion in the sulfuric acid-catalyzed reaction approaches that of the MSA-catalyzed reaction, but there are several disadvantages to using H_2SO_4 . MSA causes less dehydration of the alcohol than does sulfuric acid and, as a result, forms fewer unwanted side products and gives a higher yield. Also, the Gardner color values for both the crude and refined dioctyl phthalate are higher than when MSA is used as the catalyst. This improved color with MSA is an important advantage in plasticizer production. The product from the MSA-catalyzed reactions was easier to work up than that from either the pTSA- or H_2SO_4 -catalyzed reactions in that sharper separations, better phase clarity, and avoidance of scum at the interface were observed. This ease of purification can result in faster process cycles and higher yields.

TABLE I
ESTERIFICATION OF PHTHALIC ANHYDRIDE

Comparative Catalyst Performance for MSA, pTSA, and H₂SO₄
Reaction performed under N₂ sparge at 155-165EC

	A	B	C	D	E	F	G
Formulation (wt. %)	MSA ⁽¹⁾	MSA ⁽¹⁾	MSA ⁽¹⁾	H ₂ SO ₄	H ₂ SO ₄	pTSA	pTSA
2-ethylhexanol	51.5	51.7	51.7	51.6	51.7	51.6	51.7
Phthalic Anhydride	28.0	28.0	28.1	28.0	28.0	28.0	28.0
Toluene	20.0	20.0	20.0	20.0	20.0	20.0	20.0
MSA (100% basis)	0.55	0.28	0.19	--	--	--	--
pTSA (100% basis)	--	--	--	--	--	0.55	0.28
H ₂ SO ₄ (100% basis)	--	--	--	0.55	0.28	--	--
% Water Evolved ⁽²⁾ :							
1/4 hour	13.4%	11.6%	14.1%	15.2%	12.4%	8.0%	9.4%
1/2 hour	38.4	31.6	27.3	33.8	26.1	24.5	18.2
3/4 hour	61.0	49.7	41.4	47.5	41.0	40.0	28.3
1 hour	74.7	64.6	52.7	63.4	55.0	54.1	35.4
1 1/2 hour	86.0	80.8	63.3	79.0	77.5	72.5	47.5
2 hours	90.2	87.6	72.1	87.6	90.4	77.6	57.4
3 hours	94.7	95.3	80.0	92.0	90.7	82.6	65.3
4 hours	96.0	95.4	85.7	94.0	90.7	83.3	73.4
5 hours	96.0	97.5	86.5	94.0	90.7	83.3	75.4
Product:							
Gardner Color (Crude Product)	1-2	1-2	1	5-7	3-4	3-4	2-3
Gardner Color (Refined Product)	1	1	1	3	2	2	1-2
Specific Gravity	0.981 - 0.982	0.981 - 0.982	0.981 - 0.982	0.981 - 0.982	0.981 - 0.982	0.981 - 0.982	0.981 - 0.982
Acid Number	0.34	0.37	0.29	0.81	0.57	0.56	0.41
Approx. Raw Material Cost per pound of reactor charge - LTL drums ⁽³⁾⁽⁴⁾	\$0.29	\$0.29	\$0.29	\$0.29	\$0.29	\$0.29	\$0.29
Catalyst Cost per ⁽⁴⁾ pound of reactor charge - Bulk LTL drums	\$0.0055 \$0.0057	\$0.0028 \$0.0029	\$0.0019 \$0.0020	\$0.0003 \$0.0015	\$0.0001 \$0.0008	\$0.0026 \$0.0027	\$0.0013 \$0.0014

- (1) MSA used as 70% commercial product
(2) Percent of theory (average values for three runs)
(3) Assumes 80% recovery of toluene
(4) Prices as of December, 1982

Statistical analysis, summarized in Table II, shows that MSA gives significantly faster esterification than pTSA, whether comparisons are made on an equal weight (0.55%) or an approximately equimolar (0.28 wt % vs. 0.55 wt %) basis. (Molecular weight of MSA= 96, molecular weight of pTSA= 172.)

TABLE II

PERCENT ESTERIFICATION AFTER 2 HOURS:

0.28% MSA	87.6*	
0.55% MSA		90.2**
0.55% pTSA	77.6	77.6

* MSA different from pTSA at \$ 95% significance level.

** MSA different from pTSA at \$ 99% significance level.

Comparing equal weights of the catalysts (see Table III), MSA outperforms both pTSA and H₂SO₄.

TABLE III

PERCENT ESTERIFICATION AFTER:

	1 HOUR	2 HOURS
0.55% MSA	74.7	90.2
0.55% H ₂ SO ₄	63.4	87.6
0.55% pTSA	54.1	77.6

Comparison of the reactions using equimolar amounts of the acid catalysts shows that even at these concentrations MSA outperforms pTSA (Table IV). At these concentrations, the weight of MSA used is about half that of pTSA.

TABLE IV

PERCENT ESTERIFICATION AFTER:

	1 HOUR	2 HOURS	3 HOURS
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0.28% MSA	64.6	87.6	95.3
0.55% pTSA	54.1	77.6	82.6
0.28% H ₂ SO ₄	55.0	90.4	90.7

Although esterification in the H₂SO₄ -catalyzed reaction was slightly higher (after 2 hours) than in the MSA-catalyzed reaction, the Gardner color of the product and the ease of work-up favored the use of MSA. In all instances, the MSA-catalyzed reactions were easier to work up than those catalyzed with either pTSA or H₂SO₄. This ease of purification can be ranked as follows (easiest to most difficult):

MSA > pTSA > H₂SO₄

By incremental reductions of catalyst concentration, approximate minimal effective levels were found. For the conditions used, these were roughly 0.19% MSA (80% esterification at 3 hours, see Figure 4) and 0.55% pTSA (82.6% esterification at 3 hours, see Figure 1). There is a price premium for MSA over pTSA which fluctuates according to market conditions. This differential is negated if MSA is used at half, or less than half, the weight of pTSA.

As demonstrated above, the use of MSA provides a shorter reaction time (for equivalent conversion) than pTSA and yields a better quality product. This can be translated to an overall cost savings when MSA is used.

SUMMARY

In summary, the use of MSA as an esterification catalyst has several advantages:

- (1) More rapid esterification and consequently shorter cycle time
- (2) Improved product quality
- (3) Greater ease of purification

These advantages can lead to reduced labor and overhead costs. Since the raw-material costs per pound of finished product (ca. \$0.29/lb., January, 1983) are similar regardless of catalyst, the savings projected for labor and overhead will result in a lower net cost per pound of acceptable product when MSA is used.

All of the above advantages add up to MSA being a very attractive esterification catalyst.

MSA is a strong toxic organic acid and is corrosive to living tissue.

Acute oral toxicity in mice of anion: LD₅₀ = 6.2 grams/kg.

Method: Administered by stomach tube to mice after neutralization with sodium hydroxide.

The 1976 edition of the NIOSH Registry of Toxic Effects of Chemical Substances lists certain reaction products of methane sulfonic acid as having suspected mutagenic, teratogenic, and carcinogenic activity.

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