Ethylene glycol is seen to be the most selective solvent at the temperature studied. It also is the only solvent of the three that will permit recovery of both components pure. Its low solubility characteristics, however, require high solvent to feed ratios.

Experimental data collected for each of the three solvents studied are tabulated in Tables II and III.

ACKNOWLEDGMENT

The authors are indebted to M.R. Fenske and R.H. McCormick for their technical assistance.

LITERATURE CITED

(1) Jones, J.H., Fenske, M.R., *Ind. Eng. Chem.* **51**, 262 (1959).
(2) Treybal, R.E., Liquid Extraction, 2nd Ed., McGraw-Hill, New York, 1963.

RECEIVED for review December 6, 1962. Accepted June 17, 1963. Work supported by Esso Research and Engineering Co., and the Petroleum Research Fund, administered by the American Chemical Society. Based on theses submitted by D.G. Hutton in partial fulfillment of the M.S. degree in chemical engineering, The Pennsylvania State University, University Park, Pa., June 1960.

Effect of Contaminants on the Thermal Stability of Maleic Anhydride

C. E. VOGLER, O. B. CECIL,[1] and W. E. KOERNER
Organic Chemicals Division, Monsanto Chemical Co., St. Louis, Mo.

Heat and gas evolution data are presented for molten maleic anhydride which has been contaminated with Na^+, Li^+, K^+, Rb^+, NH_4^+, Ca^{++}, Ba^{++}, Mg^{++}, H_2O, diethylamine and triethylamine. The alkali metal ions and the alkylamines showed the largest catalytic effect. CO_2 was the principle gaseous decomposition product. The sulfate anion diminished the effect of Na^+ contamination. Na^+ had no effect on the stability of phthalic anhydride.

CONTAMINATION with sodium salts can drastically decrease the stability of maleic anhydride at elevated temperatures. Serious accidents on an industrial scale have resulted from sodium salt contamination (*7*), and the patent literature makes reference to additives designed to mitigate the effects of sodium ion contamination of maleic anhydride. Quantitative data on heat and gas evolution were needed to define more exactly the maximum sodium ion contamination that might be tolerated in the safe manufacture and use of maleic anhydride. These same data could be used to design suitable venting systems for vessels which are employed in maleic anhydride service. This paper presents quantitative data on the relationship between sodium salt concentration in maleic anhydride and heat and gas evolution rates. The influence of various anions associated with the sodium ion was studied, and the effect of other alkali metal and alkaline earth ions on the thermal stability of maleic anhydride was surveyed.

EXPERIMENTAL DETAILS

Heat and gas evolution rates were measured with a previously described differential thermal stability (DTA) apparatus with which gas evolution rates could be measured simultaneously (*1, 2*). After the sample vessel had cooled to room temperature at the end of the experiment, samples of the decomposition gases could be transferred to an infrared absorption cell for analysis.

Salt contaminated samples were prepared by pulverizing commercial maleic anhydride briquets and then dispersing the contaminant salt by careful trituration. The amine and water contaminated samples were prepared by adding the contaminant directly to the powdered maleic anhydride sample in the DTA cell.

The sodium and potassium salts of maleic acid were prepared by adding the appropriate alkali hydroxide to an aqueous solution of maleic acid to a pH of 8–9. The resultant solutions were concentrated by evaporation and cooled to crystallize the salts. The crystals were filtered and dried overnight at 130° C. and finally under vacuum. The salts prepared in this manner were assumed to be anhydrous.

The alkaline earth maleates were prepared by adding the alkaline earth chloride to an aqueous solution of maleic acid and precipitating the salt by addition of ammonium hydroxide. The resultant slurries were boiled for 10 minutes to improve the crystal form and after cooling were filtered. The crystals were washed with dilute NH_4OH and dried overnight at 130° C. and finally under vacuum. This procedure was assumed to give an anhydrous and ammonia-free product. The magnesium maleate used was already available and was not further purified for this work. Its preparation involved precipitation using NaOH and was subsequently found to contain 2.4% Na^+ as sodium maleate.

Anhydrous ammonium maleate was prepared following the procedure of Keiser and McMaster (*3*) which involved dissolving dry maleic acid in ether and bubbling dry NH_3 through the solution until no more of the diammonium salt separated. The precipitate was air dried and finally vacuum dried at room temperature to remove the remainder of the ether. The salt prepared in this manner was thermally

---

[1] Present address, Texas Instruments, Inc., Dallas, Tex.

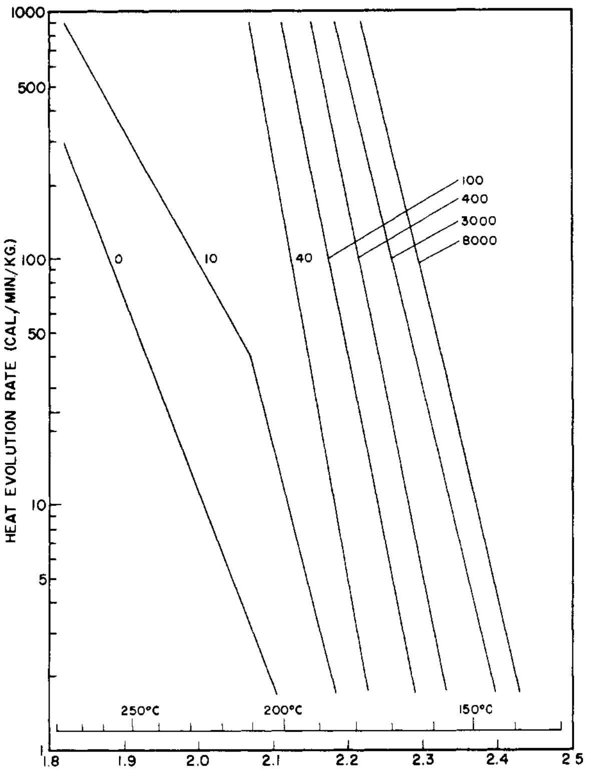

Figure 1. Heat evolution from maleic anhydride contaminated with 0–8000 p.p.m. Na^- as Na_2CO_3

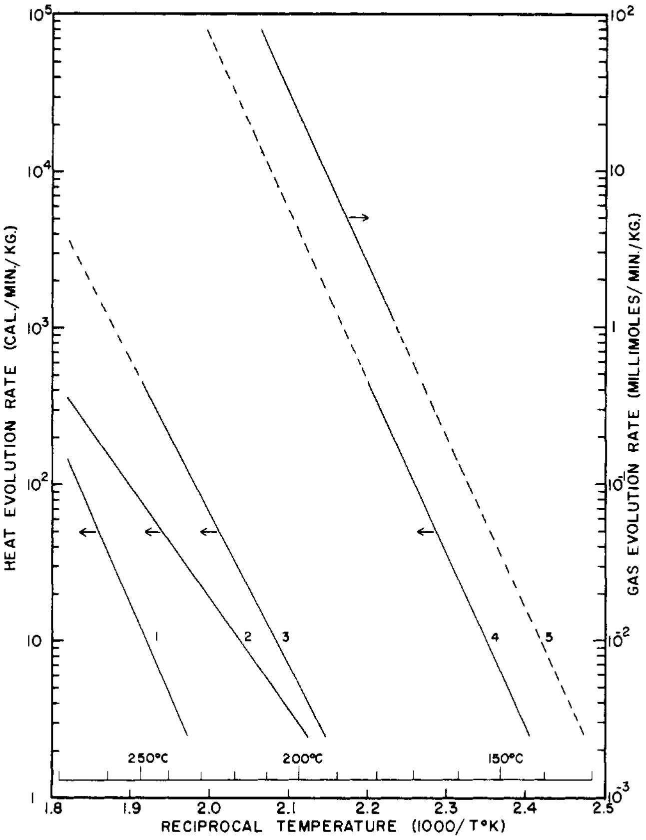

Figure 2. A. Heat evolution from:

(1) Sodium maleate
(2) Maleic anhydride
(3) Maleic anhydride contaminated with 3000 p.p.m. Na^- as Na_2SO_4
(4) Maleic anhydride contaminated with 3000 p.p.m. Na^- as sodium maleate

B. Gas evolution from:

(5) Maleic anhydride contaminated with 3000 p.p.m. Na^- as sodium maleate

stable up to 100° C. but had slight NH_3 vapor pressure at room temperature.

Commercial samples of good quality lithium carbonate, rubidium carbonate, sodium carbonate, sodium hydroxide, triethylamine and diethylamine were used in some of the experiments.

HEAT AND GAS EVOLUTION DATA

The influence of sodium ion concentration on the rate of heat evolution from contaminated maleic anhydride is shown in Figure 1 which covers the range from 0 to 8000 p.p.m. of added sodium ion as sodium carbonate. Results identical within experimental error were obtained when sodium ions were added at equimolar concentrations in the form of Na_2CO_3, NaOH, sodium maleate and $NaNO_3$. The discontinuity in the 10 p.p.m. curve in Figure 1 is real and reproducible. An exact explanation for this observation cannot be offered, but it may result from the formation of decomposition products which can tie up a significant fraction of the sodium ion mechanically or chemically. The corresponding gas evolution data are not available from this series of experiments since these data were obtained before the DTA apparatus was modified to permit the concurrent measurement of gas evolution.

Typical gas and heat evolution data from a single experiment are shown in Figure 2 for a sample of maleic anhydride contaminated with 3000 p.p.m. Na^+ as sodium maleate. The two curves are essentially parallel, suggesting that the same decomposition mechanism is responsible for both the gas and heat evolution. The data for sodium sulfate contamination in Figure 2 shows that sodium added as a very stable salt has a much diminished effect on the stability of maleic anhydride. This observation parallels information reported in the patent literature (*4, 5*) in which phosphoric acid, boric acid and boron oxide are reported to diminish the deleterious effect of sodium ion contamination.

The catalytic role of the sodium ion is shown indirectly by the data for the thermal stability of pure sodium maleate in Figure 2. Although low levels of sodium maleate in maleic anhydride greatly decrease the thermal stability of maleic anhydride, pure sodium maleate must be heated to a higher temperature than pure maleic anhydride to produce the first detectable amount of heat.

The catalytic effects of alkali metal cations and ammonium ion in the form of enhanced heat evolution are shown in Figure 3. Although the same anion was not used for all experiments, the virtual equivalence of carbonate and maleate anions with the sodium ion makes direct intercomparison of the data reasonable. On a weight basis, the order of catalytic effectiveness is $\text{K}^+ > \text{Na}^+ > \text{Rb}^+ > \text{Li}^- > \text{NH}_4^-$. When the catalytic effectiveness of the ions is compared on a molar basis to gain a better insight into the role of ion basicity, the order is $\text{Rb}^- > \text{K}^- > \text{Na}^+ > \text{Li}^- > \text{NH}_4^-$. This is the same order as the relative basicity or electropositivity of these ions. The corresponding gas evolution data from these experiments is shown in Figure 4.

The effect of alkaline earth metal cations on the heat evolution from maleic anhydride is shown in Figure 5. Discontinuities similar to that shown in Figure 1 for the 10 p.p.m. curve were observed in the alkaline earth contamination studies. The data shown in Figure 5 represent the first segment of the curve. Extrapolation of this segment of the curve yeilds the highest possible heat evolution rate and thus provides a conservative basis for safety considerations. As a group, the alkaline earth cations have little effect on the thermal stability of maleic

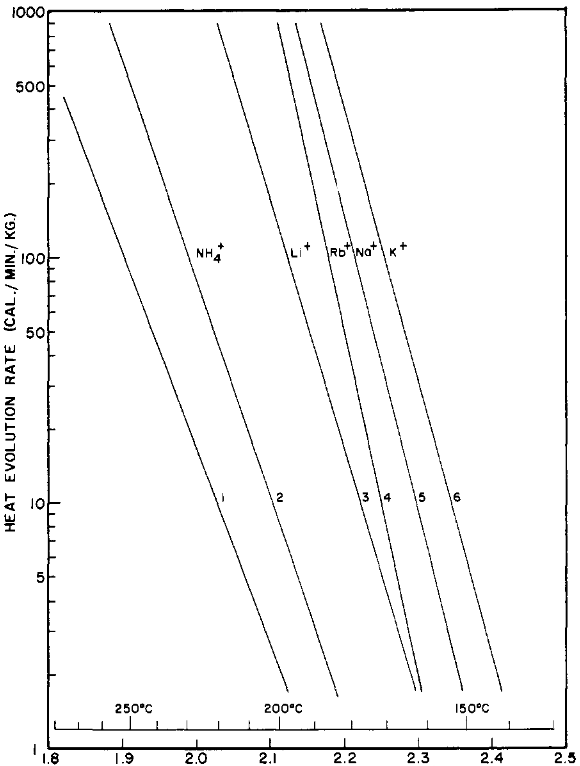

Figure 3. Effect of alkali metal cations on heat evolution from maleic anhydride

(1) Maleic anhydride alone
(2) 400 p.p.m. NH_4^- as ammonium maleate
(3) 400 p.p.m. Li^- as lithium carbonate
(4) 390 p.p.m. Rb^+ as rubidium carbonate
(5) 400 p.p.m. Na^- as sodium maleate
(6) 400 p.p.m. K^- as potassium maleate

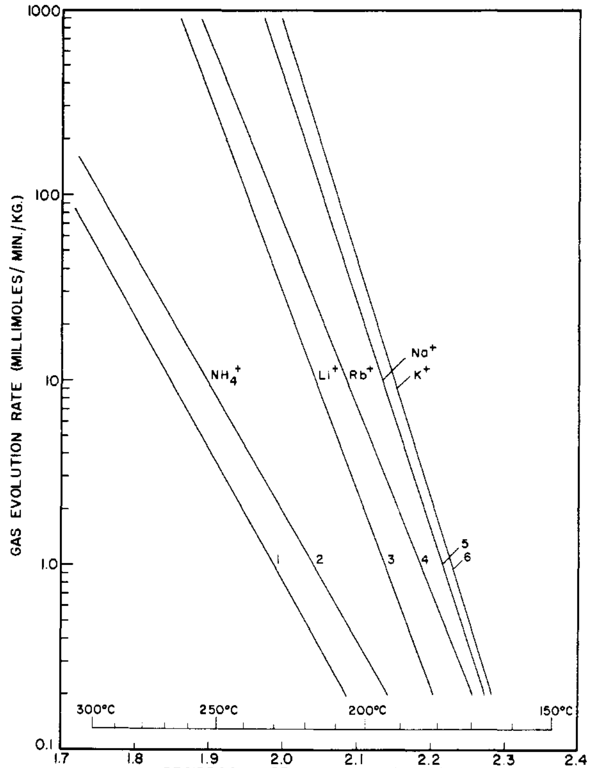

Figure 4. Epect of alkali metal cations on gas evolution from maleic anhydride

(1) Maleic anhydride alone
(2) 400 p.p.m. NH_4^- as ammonium maleate
(3) 400 p.p.m. Li^+ as lithium carbonate
(4) 390 p.p.m. Rb^- as rubidium carbonate
(5) 400 p.p.m. Na^- as sodium maleate
(6) 400 p.p.m. K^- as potassium maleate

anhydride as compared to the alkali metal ions. There is little correlation with the electropositivities of the ions. Barium is about as electropositive as sodium but does not even approximate the catalytic action of sodium. The sodium ion contaminant in the magnesium maleate prevented accurate measurement of the magnesium ion effect. By estimating the heat evolution contribution from the sodium ion using the data from Figure 1 and assuming that the effects of the two ions are additive, the magnesium ion was shown to have little effect on the stability of maleic anhydride. Gas evolution data from the alkaline earth ion experiments are also shown in Figure 5, and, in general, parallel the heat evolution data.

Data for the effect of triethylamine, diethylamine and water on the gas and heat evolution from maleic anhydride are presented in Figure 6. Triethylamine and diethylamine which are relatively strong organic bases are about equivalent to sodium ion in catalytic effectiveness. Very rapid decomposition of maleic anhydride at elevated temperatures in the presence of pyridine or quinoline has also been encountered (*6*). When triethylamine was added to maleic anhydride at room temperature, a deep red intermediate was formed which decomposed on heating. This color reaction appears to be a general one with tertiary amines (*8*) and does not occur with primary and secondary amines. The presence of water in maleic anhydride can be seen to decrease the stability of maleic anhydride. Probably the water reacts to form maleic acid which can undergo thermal decarboxylation at elevated temperatures. Some evidence for the existence of a two-segment decomposition curve was observed in the water experiment and it is the low temperature segment that is shown in extrapolated form in Figure 6.

CHEMISTRY OF THE DECOMPOSITION

The gases produced by the thermal decomposition of maleic anhydride, both catalyzed and non-catalyzed, in the DTA runs were analyzed by infrared absorption. The spectra of the gases showed that predominately CO_2 was produced, with only trace amounts of CO and low boiling hydrocarbon fragments present. Probably the maleate ion is formed whose ease of decarboxylation would be dependent upon the basicity of the cation. Upon decarboxylation, an active monomer is formed which could react with maleic anhydride or other monomer molecules ultimately to form a high polymer. The effect of water upon the thermal stability of maleic anhydride would support this mode of reaction.

The solid product of the decomposition of maleic anhydride was isolated by removal of unreacted maleic anhydride by chloroform extraction. The infrared spectra of the solid sample was not much different than that of maleic anhydride still showing strong carboxyl group absorption. The solid product appears to be a heterogeneous polymer having an average molecular weight of 400-500 as determined by the molal boiling point elevation of acetone. The solid product was fractionated by precipitation from acetone solution by the addition of ether. The less soluble fraction was separated and dried. The average molecular weight of this fraction was found to be 1030.

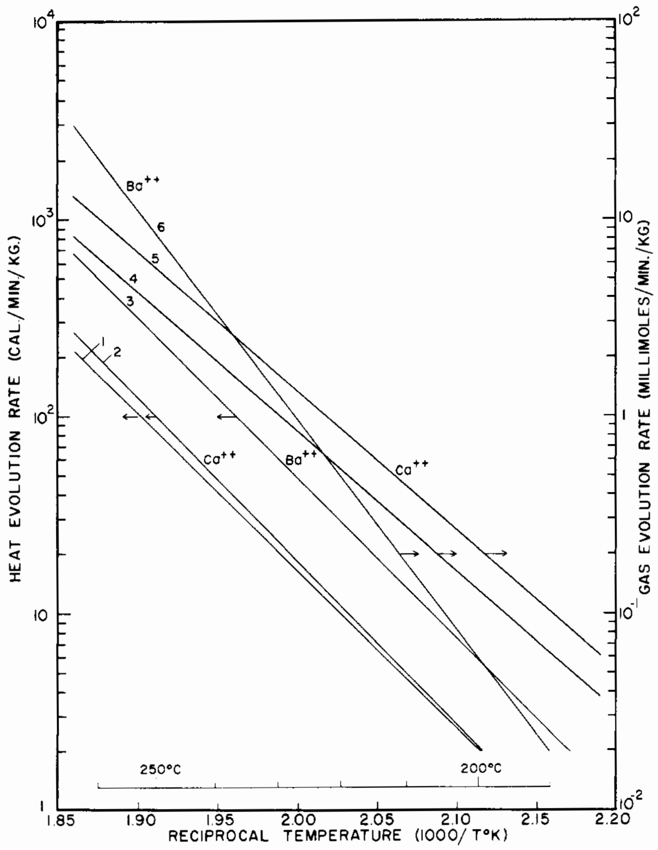

Figure 5. Effect of calcium and barium ions on heat and gas evolution from maleic anhydride

Heat (1) Maleic anhydride alone
(2) 4000 p.p.m. Ca^{--} as calcium maleate
(3) 4000 p.p.m. Ba^{--} as barium maleate

Gas (4) Maleic anhydride alone
(5) 4000 p.p.m. Ca^{--} as calcium maleate
(6) 4000 p.p.m. Ba^{-+} as barium maleate

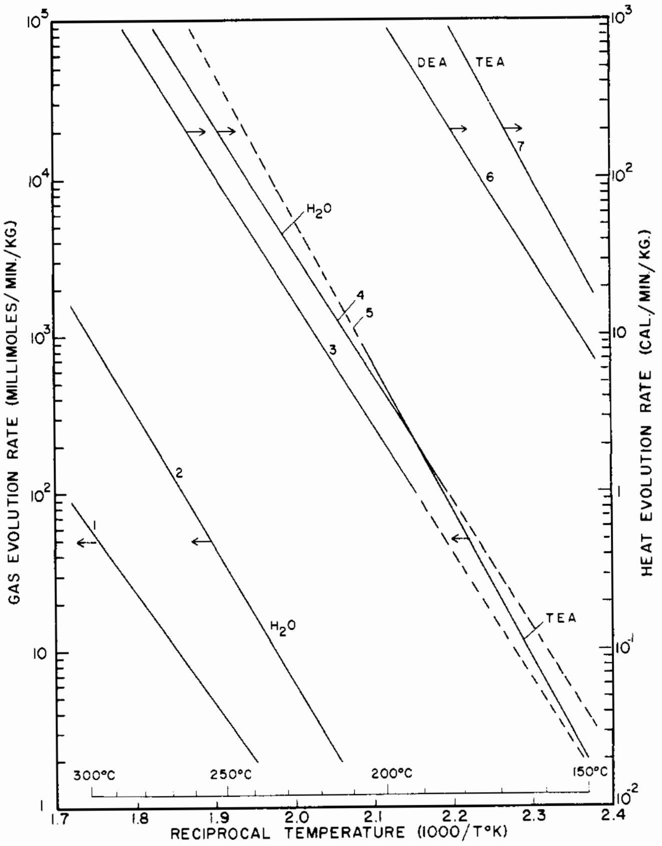

Figure 6. Effect of water and amines on gas and heat evolution from maleic anhydride

Gas (1) Maleic anhydride alone
(2) 1.33% water (equivalent to 8.57% maleic acid)
(4) 3690 p.p.m. triethylamine

Heat (3) Maleic anhydride alone
(5) 1.33% water (equivalent to 8.57% maleic acid)
(6) 2350 p.p.m. diethylamine
(7) 3690 p.p.m. triethylamine

EXPERIMENTS WITH PHTHALIC ANHYDRIDE

A thermal stability experiment with phthalic anhydride showed that contamination with 2000 p.p.m. sodium ion exhibited no appreciable heat evolution up to 280° C., the termination point of the experiment. The presence of phthalic anhydride was also shown not to enhance the instability of contaminated maleic anhydride when contaminated mixtures of the two anhydrides were subjected to DTA.

ACKNOWLEDGMENT

The assistance of H.W. Luebke in carrying out some of the thermal stability experiments and of O.E. Kinast in the infrared examination of the decomposition gases and products is gratefully acknowledged.

LITERATURE CITED

(1) Cecil, O.B., Koerner, W.E., *Ind. Eng. Chem.* **53**, 475 (1961).
(2) Deason, W.R., Koerner, W.E., Munch, R.H., *Ibid.*, **51**, 997 (1959).
(3) Keiser, E.H., McMaster, L., *Am. Chem. J.* **49**, 84 (1913).
(4) Kohn, G.K., (to California Spray-Chemical Corp.), U. S. Patent **2, 831,869** (April 22, 1958).
(5) Kohn, G.K. (to California Spray-Chemical Corp.), U. S. Patent **2,863,880** (December 9, 1958).
(6) Kohn, G.K., California Spray-Chemical Corp., Richmond, California, private communication, 1963.
(7) Manufacturing Chemists Association, Case History No. **622**, May 25, 1960, Washington, D. C.
(8) Rittenberg, D., Ponticorvo, L., *Proc. Nat'l Acad. Sci. U. S.* **46**, No. 6, 822 (1960).

RECEIVED for review December 6, 1962. Accepted June 17, 1963.