

The mechanic study of the Pd-catalyzed synthesis of diphenylcarbonate with heteropolyacid as a cocatalyst

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Abstract

The reaction to synthesize diphenyl carbonate (DPC) by an oxidative carbonylation of phenol with CO and O₂ has been found to proceed through the second-order of phenol concentration. The activation energy E_a , ΔS and ΔH are 27.0 kcal mol⁻¹, -6.43 cal mol⁻¹ and 26.3 kcal mol⁻¹, respectively. The kinetic and additive data obtained agree with the proposed mechanism as follows: Pd(OAc)₂ reacts with an ammonium phenoxy salt to give AcO-Pd-OPh which then reacts with CO to form AcO-Pd-COOPh. This species leads to PhO-Pd-COOPh which undergoes reductive elimination to give DPC and Pd(0). This Pd(0) is reoxidized to Pd(II) by the help of a heteropolyacid very effectively.

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1. Introduction

Diphenyl carbonate (DPC), an important precursor of polycarbonate, is industrially produced by the reaction of phenol and phosgene with a formation of chlorinated waste [1]. In recent years, there is an increasing demand for a safer process of DPC manufacture. Oxidative carbonylation of phenol with CO and O₂ is one of the attractive processes in which the use of toxic phosgene is avoided as in Eq. (1).



In the previous literature, many metal compounds were chosen as catalysts for the oxidative carbonylation reaction [2–11] and palladium was thought to be the most active catalyst. In this reaction, regeneration of Pd(II) from Pd(0) is the crucial step for the high yield of DPC and high turnover number (TON) of Pd. However,

direct oxidation of Pd(0) to the Pd(II) species with oxygen was confirmed to be very slow, which results in an aggregation of Pd(0) to form palladium black that is more difficult to reoxidize to Pd species from Pd(0). Therefore, the efficient redox cocatalysts are essential to achieve a rapid reoxidation of Pd(0). It was reported that heteropolyacids (HPAs) could act as a redox cocatalyst in some palladium-catalyzed reactions [12,13]. We also reported the highly effective HPA cocatalysts for the catalytic carbonylation of phenol with CO and O₂ [14,15].

In this process, TON of Pd(OAc)₂ increased diametrically [15]. The amount of Pd found as palladium black decreased clearly in the high TON reactions compared with low TON reactions. It was also known that Pd catalyst system to use ammonium halides gave the best efficiency [5]. However, it is not yet known why halides gave the best efficiency. It is also known that an HPA acts as a redox cocatalyst against Pd through Mn metals [15]. To elucidate the optimum amount of Mn, ammonium salts and HPAs are very important and requisite for not only to improve the productivity of DPC and

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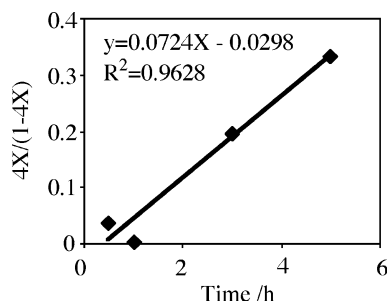


Fig. 1. The reaction order (second-order). Conditions: phenol, 0.5 mol; Pd(OAc)₂, 0.16 mmol; (TBA)₄SiW₆Mo₆O₄₀, 0.047 mmol; TBAB, 3.0 mmol; M.S. 3A, 7.0 g; total pressure, 8 atm; CO, 500 ml min⁻¹; O₂, 35 ml min⁻¹; 80 °C, 3 h.

TON of Pd, but also to find out a plausible active catalyst and reaction mechanism for this reaction. In addition to the kinetic data for this reaction, these experiments were performed. By these experiments, we could understand this reaction well. Here we report the results and propose the reaction mechanism.

2. Results and discussion

2.1. Kinetic analysis of DPC production in the Pd–HPA catalyst system

Kinetic study was done using the flow system under the conditions of 80 °C and total pressures of 8 atm by adding Pd(OAc)₂, (NBu₄)₄SiW₆Mo₆O₄₀ ((TBA)₄SiW₆Mo₆O₄₀), tetrabutylammonium bromide (TBAB) and molecular sieves (M.S.) to the system. The DPC yield (*X*) was obtained against time. These data were analyzed to give the best-fit for the second-order reaction against phenol with $R^2 = 0.9628$ as shown in Fig. 1. This result means that the reaction proceeds in the second-order of phenol; phenol reacting with another phenol containing active species at the rate-determining step. The calculated data fitted with the experimental ones as shown in Fig. 2.

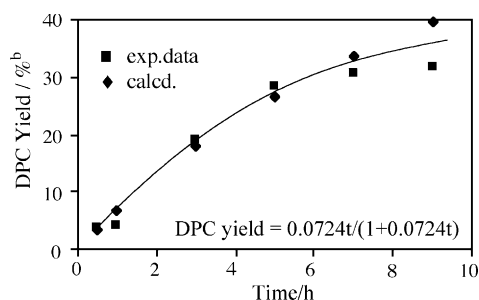


Fig. 2. Comparison of experimental data with calculated data. Conditions: phenol, 0.5 mol; Pd(OAc)₂, 0.16 mmol; Mn(OAc)₂, 0.32 mmol; (TBA)₄SiW₆Mo₆O₄₀, 0.047 mmol; TBAB, 3.0 mmol; M.S. 3A, 7.0 g; total pressure, 8 atm; CO, 500 ml min⁻¹; O₂, 35 ml min⁻¹; 80 °C, 3 h. Determined by GC. DPC yield (%) = 2 × (DPC produced, mol)/(reacted phenol, mol) × 100.

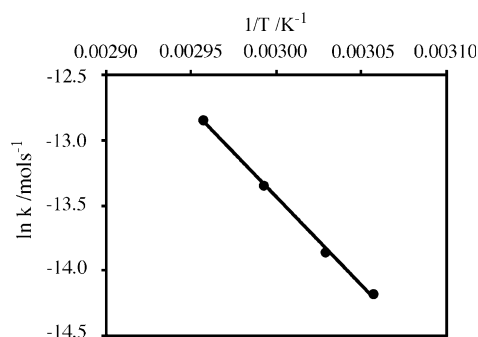


Fig. 3. Arrhenius plot of DPC. Conditions: phenol, 0.5 mol; Pd(OAc)₂, 0.16 mmol; TBAB, 3.0 mmol; (TBA)₄SiW₆Mo₆O₄₀, 0.047 mmol; total pressure, 8 atm; CO, 500 ml min⁻¹; O₂, 35 ml min⁻¹; M.S., 7 g; 0.5 h. *k* is the production rate of DPC (mol s⁻¹).

2.2. Arrhenius plot of DPC production

Arrhenius plots were obtained in the temperature range 327–338 K. These data were shown in Fig. 3 to give $E_a = 27.0$ kcal mol⁻¹, $\Delta S = -6.43$ cal mol⁻¹ and $\Delta H = 26.3$ kcal mol⁻¹, respectively. The negative entropy obtained means that some type of complex is formed at the rate-controlling step [16]. The positive enthalpy means that this reaction can be effectively performed even under 373 K in the industrial scale.

2.3. Effect of TBA salts

The effect of change of anion of TBA salts is also an interesting aspect. Table 1 summarizes these results. It can be concluded that only bromide causes this reaction effectively. Other anions could not cause this reaction at all. In order to understand this phenomenon clearly, we plotted DPC yield against pK_a of conjugated acids. The result is shown in Fig. 4. This figure clearly shows that pK_a of a conjugated acid is important in this reaction and should be lower than -8 . If the pK_a of the conjugated acid is lower than -8 , we would be able to get a good DPC yield. HI has a lower pK_a than -9 . However I⁻ is easily oxidized by oxygen to I₂ [2]. Therefore ammonium iodide is not appropriate. This

Table 1
Effect of TBA salt (anion part)^a

Entry	TBA salt	Yield (%) ^b	TON ^c
1	TBA-Br	20.8	325
2	TBA-Cl	2.0	33
3	TBA-F·3H ₂ O	0.1	1
4	TBA-CN	Trace	—
5	TBA-OAc	Trace	—

^a Conditions: phenol, 0.5 mol; Pd(OAc)₂, 0.16 mmol; (TBA)₄SiW₆Mo₁₁O₄₀, 0.047 mmol; Mn(OAc)₂, 0.32 mmol; TBA salts, 3.0 mmol; M.S., 7.0 g; total pressure, 8 atm, CO, 500 ml min⁻¹; O₂, 35 ml min⁻¹; 80 °C, 3 h.

^b GC yield based on charged phenol.

^c TON based on Pd.

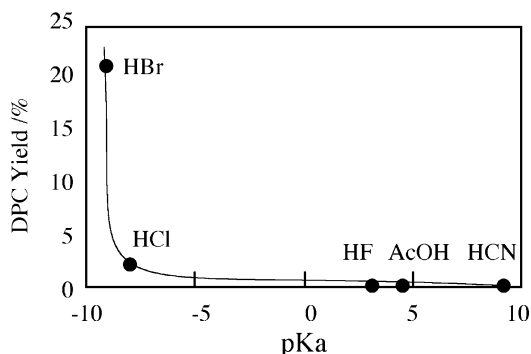


Fig. 4. DPC yield and pK_a of conjugated acid of TBA salts.

result suggests that the use of the ammonium salt of an HPA with the conjugated acid's pK_a lower than -9 gives a good result. When negative entropy and the addition of a large amount of ammonium salt are considered in this reaction, a plausible active complex may be formed with Pd, Mn, HPA, tetraalkylammonium cation and PhO^- . These results support that the best coordination to form phenoxy salt for the production of DPC is only achieved by bromide anion. Other simple anions are inferior to bromide anion in this sense.

2.4. Effect of NaBr

The addition of NaBr to the reaction system was investigated as shown in Table 2. The addition of NaBr instead of tetraalkylammonium salt decreased the production of DPC dramatically. It almost prevents the reaction. NaBr might decrease the formation of a phenoxy ammonium salt which would be a very effective intermediate. Therefore, the formation of phenoxy salt is requisite for this reaction. Addition of a large amount of NaBr caused a difficulty of agitation to give an inferior result.

2.5. Effect of the amount of an amine and ammonium salts on Pd TON

It is also important to investigate the effect of the amount of an amine and an ammonium salt to under-

Table 2

Effect of $\text{Pd}(\text{OAc})_2$, amount of $\text{Mn}(\text{OAc})_2$, HPA, NaBr ^a			
$2 \text{ PhOH} + \text{CO} + 1/2 \text{ O}_2 \xrightarrow[80^\circ\text{C}, 3\text{ h}]{\text{Pd}(\text{OAc})_2, \text{Mn}(\text{OAc})_2, \text{HPA}} \text{Ph}-\text{O}-\text{C}(=\text{O})-\text{O}-\text{Ph} + \text{H}_2\text{O}$			
Entry	NaBr (mmol)	Yield (%) ^b	TON ^c
1	3	0.83	12.8
2	30	0.23	3.8
3	—	22.7	354

^a Conditions: phenol, 0.5 mol; $\text{Pd}(\text{OAc})_2$, 0.16 mmol; $\text{Mn}(\text{OAc})_2$, 0.32 mmol; $(\text{TBA})_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$, 0.05 mmol; TBAB, 3 mmol; M.S., 7 g; THF, 15 ml min^{-1} ; 8 atm; CO, 670 ml min^{-1} ; O_2 , 47 ml min^{-1} ; 80 °C, 9 h.

^b GC yield based on charge phenol.

^c TON based on Pd.

stand the reaction mechanism. Fig. 5 gives these results. From this figure, one can see that Bu_3N gives a very slow and low values of TON. On the contrary, TBAB gives a rather higher TON. This means that an easy coordination of a salt to form a phenoxy salt helps to attain a higher TON. It may be necessary first to form a phenoxy salt to proceed the reaction. In this sense, Bu_3N seems difficult to form a phenoxy salt.

2.6. Influence of the amount of $\text{H}_3\text{PW}_6\text{Mo}_6\text{O}_{40}$, $\text{Mn}(\text{OAc})_2$ and TBA salt

Then we investigate the effect of the amount of $\text{H}_3\text{W}_6\text{Mo}_6\text{O}_{40}$ on the DPC product. The results are shown in Fig. 6. DPC production increased until the amount was 0.047 mmol and stayed constant until 0.06 mmol, then decreased rather sharply with the increase of the amount of HPA. The rather sharp decrease may be caused due to the difficult solubility of HPA to the system. The optimum amount of Mo to Pd is around 2.2–2.8, a little bit smaller than 3. This number shows that about three Pd may be combined with 1 mol of HPA to form an optimum active catalyst. The optimum amount of Mn to Pd is 2 as shown in Fig. 7. The optimized amount of the ammonium salt to HPA is around 100 as shown in Fig. 8. In combination with these results, we may be able to induce a general idea of the active complex. It is shown in Fig. 9. In this figure, Pd shows Pd metal or a variety of Pd(II) complexes to avoid complexity. Mn also shows Mn(II) or Mn(III) complexes. More oxonium ions are thought to be bound to Mo (or W) of HPA or Mn ions actually. In order to get a high turnover of Pd catalyst and a high yield of DPC, It is requisite that the catalyst system is dissolved in the reaction system. This was attained by an HPA and a tetraalkylammonium salt by the formation of an active catalyst complex. An HPA and a tetraalkylammonium salt are important. Pd metal in the complex does not form Pd metal cluster which is not easily reoxidized to Pd(II). Pd metal in the complex must be coordinated by HPA. In this sense Pd(0) may be bound to O atoms in HPA. Mn ion is also combined with HPA in the same way as in Pd. So the electron pumping from Pd(0) to

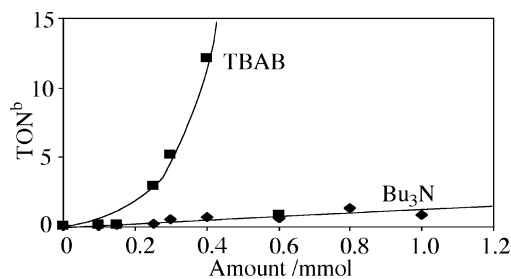


Fig. 5. Relations of the amount of amines vs TON. Conditions: phenol, 50 mmol; $\text{Pd}(\text{OAc})_2$, 0.016 mmol; $\text{Mn}(\text{OAc})_2$, 0.032 mmol; $\text{H}_3\text{PW}_6\text{Mo}_{11}\text{O}_{40}$, 0.0047 mmol; M.S., 0.7 g; mixture gas ($\text{CO}:\text{O}_2 = 11:1$), 40 ml min^{-1} ; 80 °C, 3 h. GC yield based on $\text{Pd}(\text{OAc})_2$.

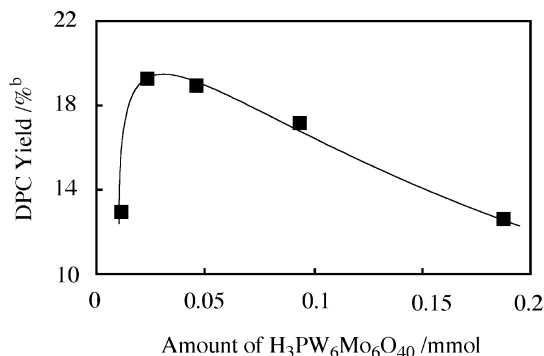


Fig. 6. The influence of the amount of $\text{H}_3\text{PW}_6\text{Mo}_6\text{O}_{40}$ on the reaction. Conditions: phenol, 0.5 mol; $\text{Pd}(\text{OAc})_2$, 0.16 mmol; $\text{Mn}(\text{OAc})_2$, 0.32 mmol; TBAB, 3.0 mmol; M.S. 3A, 7 g; total pressure, 8 atm; CO , 500 ml min^{-1} ; O_2 , 35 ml min^{-1} ; 80 °C, 3 h. Determined by GC.

Mn^{3+} may be done through O atoms. The solubility of the active complex may be controlled by the number of the combined ammonium cations on the active complex. The more the ammonium cations attach to the complex, the more it becomes soluble in the system. The more the number of cations around the complex, the more it may attract the phenoxy ion around Pd and induces high yield of DPC and high TON of Pd. The production of very small amount of CO_2 and high selectivity of DPC in this system also support the coordination of Mn to HPA anion. The oxidation of HPA may be occurring through the combination of Mo (or W) and O_2 in the ordinary manner [15].

Based on the results obtained so far, we propose the following mechanism (Fig. 10). In this figure, only the real catalytic part of Pd is shown. To understand the catalytic situations, it is better to replace each Pd in Fig. 9 with each of the Pd complexes (A)–(E) in Fig. 10 depending on the complex mentioned. The acetate ligand anion in $\text{Pd}(\text{OAc})_2$ is replaced by a phenoxy anion of a tetraalkylammonium phenoxide to give a PhO-Pd salt [2]. It allows to induce carbonylation by CO to give a PhOCO-Pd-OAc complex. This species undergoes a further replacement of an acetate anion to

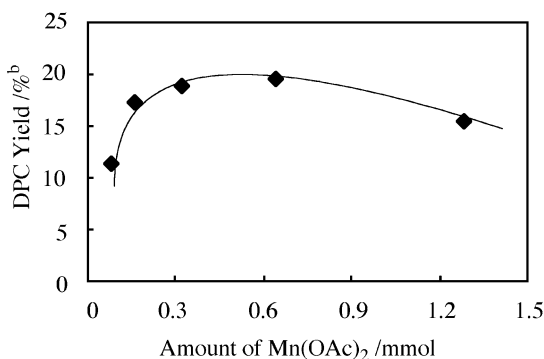


Fig. 7. The influence of the amount of $\text{Mn}(\text{OAc})_2$ on the reaction. Conditions: phenol, 0.5 mol; $\text{Pd}(\text{OAc})_2$, 0.16 mmol; $\text{H}_3\text{PW}_6\text{Mo}_6\text{O}_{40}$, 0.05 mmol; TBAB, 3.0 mmol; M.S. 3A, 7 g; total pressure, 8 atm; CO , 500 ml min^{-1} ; O_2 , 35 ml min^{-1} ; 80 °C, 3 h. Determined by GC.

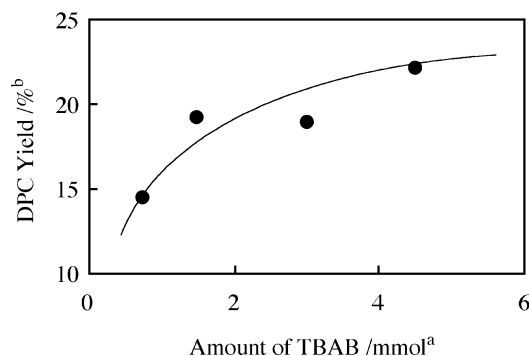


Fig. 8. The influence of the amount of TBAB on the reaction. Conditions: phenol, 0.5 mol; $\text{Pd}(\text{OAc})_2$, 0.16 mmol; $\text{H}_3\text{PW}_6\text{Mo}_6\text{O}_{40}$, 0.05 mmol; $\text{Mn}(\text{OAc})_2$, 0.32 mmol; M.S. 3A, 7 g; total pressure, 8 atm; CO , 500 ml min^{-1} ; O_2 , 35 ml min^{-1} ; 80 °C, 3 h. Determined by GC.

give PhOCO-Pd-OPh . This complex further experiences reductive elimination to give $\text{Pd}(0)$ and DPC. The $\text{Pd}(0)$ would be reoxidized to $\text{Pd}(\text{II})$ by the process shown in the literature [15]. The experiments to prove the formation of phenoxy salt from phenol and ammonium salt, and the proof of CO complex formation are now under investigation.

3. Conclusion

The reaction to synthesize DPC by an oxidative carbonylation of phenol with CO and O_2 proceeds through the second-order of PhOH concentration. The activation energy E_a , ΔS and ΔH are 27.0 kcal mol^{-1} , $-6.43 \text{ cal mol}^{-1}$ and 26.3 kcal mol^{-1} , respectively. The values obtained in experiments agree with the proposed mechanism as follows: $\text{Pd}(\text{OAc})_2$ reacts with an ammonium phenoxy salt to give AcO-Pd-OPh which then reacts with CO to form AcO-Pd-COOPh . This species leads to PhOCO-Pd-OPh that undergoes reductive elimination to give DPC and $\text{Pd}(0)$. $\text{Pd}(0)$ is reoxidized to $\text{Pd}(\text{II})$ by the help of an HPA very effectively.

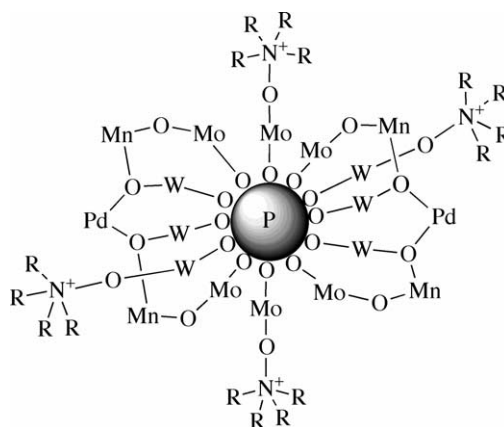


Fig. 9. Image diagram of the active catalyst.

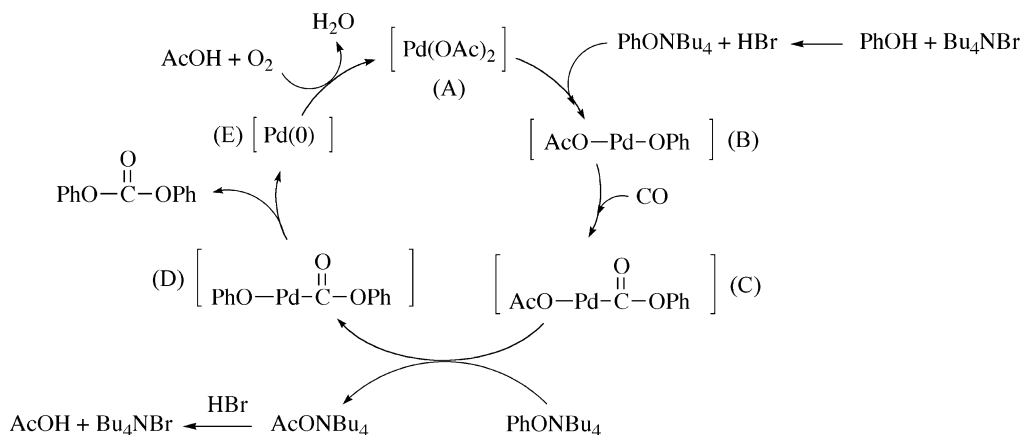


Fig. 10. Possible mechanism.

4. Experimental

(TBA)SiW₆Mo₆O₄₀ and (TBA)SiMo₁₁O₄₀ were synthesized according to the reported method [17]. All other reagents were obtained from commercial sources and used as received. Molecular sieve (M.S.) was activated at 450 °C in air for 10 h before use. All the reactions are run in an autoclave by flow system except the one done for Pd TON using tributylamine and TBAB under a normal pressure.

A typical reaction procedure is as follows: $\text{Pd}(\text{OAc})_2$ (0.036 g, 0.16 mmol), $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.078 g, 0.32 mmol), (TBA)SiW₆Mo₆O₄₀ (0.047 mmol), TBAB (1 g, 3 mmol), 3A powder M.S. (7 g) and hot phenol (47 g, 0.5 mol) were charged in a 100-ml stainless steel autoclave which was kept at 60 °C. In case of Arrhenius plotting experiments, the reactor was first heated to and kept at the reaction temperature. The autoclave was then sealed. With mechanical stirring at 800 rpm, a gas mixture (6.5 mol% O_2 and 93.5 mol% CO) was introduced into the autoclave at a flow rate of 535 ml min^{-1} and the autoclave was heated to 80 °C. The pressure of the autoclave was kept at 8 atm with continuous gas flow for the desired time. After the reaction, the pressure was reduced to an atmospheric pressure, and the gas mixture was exchanged with nitrogen. Then, the hot reaction solution was transformed into a receiver and 30 ml of EtOAc was used to wash the autoclave. Finally, the solutions were combined and analyzed by GC with a capillary column (DB-1, 15 m $\times$ $\varnothing$ 0.53 mm, J & W Scientific). The products were identified by NMR spectra (JEOL, JNM-AL300). The major side products were phenylsalicylate and 4-phenoxy phenol. The yield of DPC is based on the charged phenol and determined by GC using diphenyl as an internal standard and is listed in the tables. The selectivity is based on the DPC percentage in the products evaluated from the peak areas on the GC chart.

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