DIFFERENTIAL ELECTROLYTIC POTENTIOMETRY: MARK-SPACE BIASED PERIODIC POLARIZATION IN SUBSTITUTION, ADDITION, AND OXIDATION TITRIMETRY IN PROPYLENE CARBONATE

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الخلاصة :

لقد تم في هذا البحث تطبيق الطريقة التفاضلية لقياس فرق الجهد الكهربائي والمعتمدة على استخدام الموجة المربعة ذات الاختلاف الزمني في دراسة تفاعلات الاستبدال والإضافة والأكسدة باستخدام كربونات البروبيلين كمذيب . وخلافاً للنتائج السابقة التي اعتمدت على طرق أخرى ، فلقد أثبتت هذه الدراسة عدم إمكانية المعايرة المباشرة لكل من الفينولات والأمينات والأوليفينات ، ويتضح من منحنيات المعايرة الناتجة بأن تفاعلات هذه المركبات مع البروم تعتبر بطيئة كما هي الحال في أكسدة حامض الأسكوربيك . لهذا لا يمكن القول باستخدام طريقة فرق الجهد العادية ولا الطريقة التفاضلية التي تعتبر أكثر دقة من الطريقة العادية لدراسة تفاعلات المركبات المذكورة مع البروم في كربونات البروبيلين .

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ABSTRACT

The application of mark-space biased square wave differential electrolytic potentiometry to substitution, addition, and oxidation reactions in propylene carbonate has been studied for the first time. In contrast to previous results using other techniques, the direct titration of phenols, amines, and olefins with bromine was found to be rather difficult. The titration curves obtained indicate that the reactions of these compounds with bromine are slow. In the case of bromination of phenols, pyridine was found to have a slight catalytic effect. The oxidation of L-ascorbic acid was also found to be slow. Therefore, neither classical potentiometry nor the more sensitive mark-space biased differential electrolytic potentiometry can be recommended for bromination reactions of the above-mentioned compounds in propylene carbonate.

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INTRODUCTION

The technique of mark-space biased periodic differential electrolytic potentiometry (msb DEP) enhances the response speed of the electrodes, sustains their activity and does not require a reference half-cell. Hence, it is suitable for nonaqueous titrations. This technique has been successfully applied to acid–base reactions in acetic anhydride–acetic acid mixtures [1] and to precipitation reactions in anhydrous acetic acid [2]. The technique has also been applied to bromination and oxidation–reduction reactions in anhydrous acetic acid [3]. It has been found that the reactions of bromine with phenols are slow even in the presence of a catalyst such as pyridine [3].

Various workers have employed pyridine to catalyse the bromination of phenols. Ingberman [4] found that bromination of phenols in glacial acetic acid was complete in 20 minutes if a certain amount of pyridine is present. Huber and Gilbert [5] have titrated several phenols with bromine using a mixture of 90% glacial acetic acid and 10% pyridine as a medium for their titrations. Kratochvil and others [6] have applied the same catalyst for the direct titrations of phenols and aromatic amines in propylene carbonate (PC). It has been reported that pyridine acts as a base in PC and it catalyses the bromination of phenols to an extent which allows their direct titration with bromine. PC has also been used as a medium for the direct titration of olefins with bromine [7]. It has been reported that the addition reactions are rapid in PC and can be followed directly by potentiometry.

EXPERIMENTAL

The polarization source, the titration cell and the procedure have all been described elsewhere [1–3]. Propylene carbonate (BDH Chemicals) and chloroform (BDH Chemicals) were purified according to previously described methods [6, 7]. The procedures of the preparation and standardization of the bromine solution, the preparation of phenols, oxidation indicators and fatty acids have also been described [3, 6, 7]. A solution of 0.01M L-ascorbic acid was prepared by dissolving the required weight in a small amount of warm acetic acid and then diluting the solution to the proper volume with PC. The supporting electrolyte was prepared by dissolving the required weight of anhydrous lithium perchlorate in PC. The molarity of this solution was 0.05M.

RESULTS AND DISCUSSION

Initial studies were aimed at titrating phenol, *p*-nitrophenol, and *p*-chlorophenol directly with bromine. Three equivalents of pyridine were added per equivalent of each of these compounds in order to catalyze their bromination [6]. The direct titration of these compounds, however, was found to be impossible because their reactions with bromine are slow in spite of the presence of pyridine. In an attempt to follow the bromination of these compounds in PC, the method of double excess back titration [3] was adopted. The results of this method are shown in Table 1, which indicates the slow reactions with bromine.

Table 1. Bromination of Phenols in PC

Sample*, mmol.	Time of standing, h	mmol of Br_2 consumed
Phenol	6	0.180
	16	0.250
	22	0.302
p-nitrophenol	6	0.120
	22	0.203
p-chlorophenol	6	0.142
	22	0.241

*A 0.1 mmole sample was taken

The bromination of thymol and hydroquinone has been found to be faster than that of phenol in acetic acid [3]. Direct titration of these compounds was also attempted in PC. Although interpretable curves were observed (Figure 1a and 1b), each of these titrations was found to last more than 3 hours. This is evident from the shapes of the differential curves (Figure 1a and 1b), which do not show sharp peaks at the end-points. However, the end-points can be located by extrapolating the lines on either side of the first break of each differential curve. The points of intersection

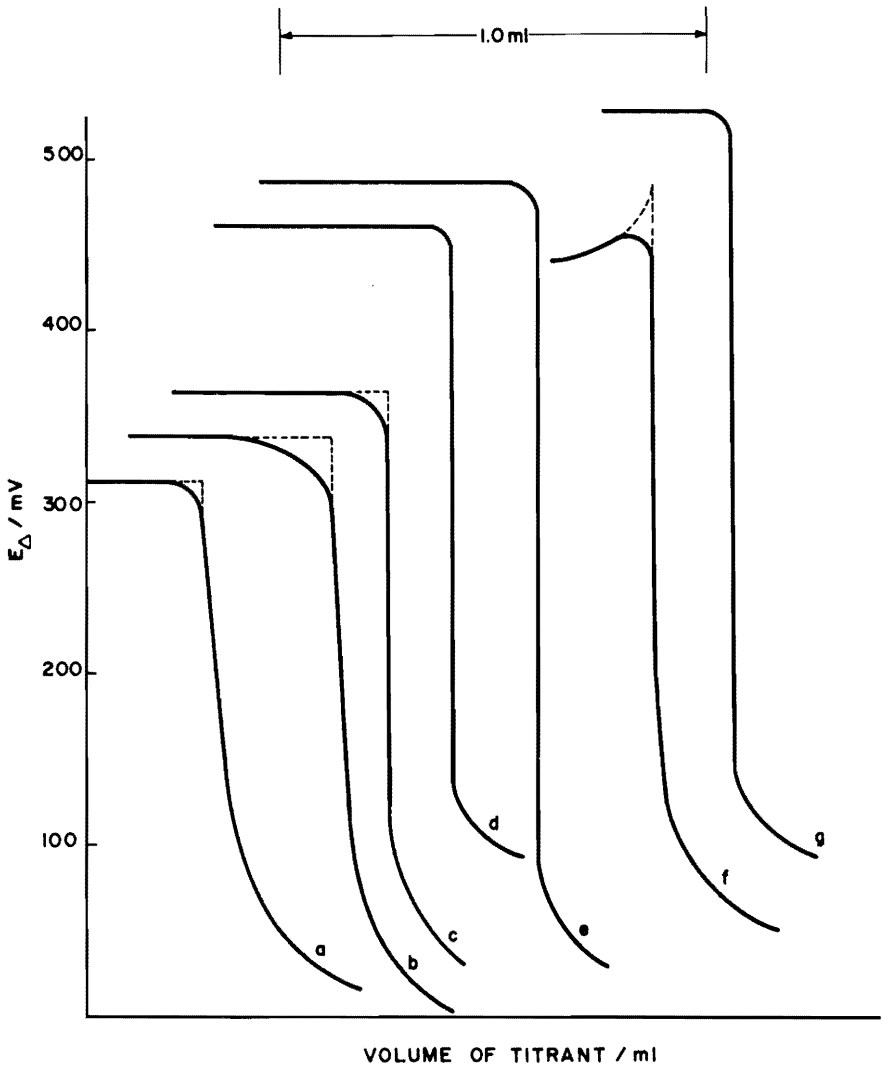

Figure 1. Msb Differential Curves of Phenols Using Platinum Electrodes. Percentage Bias = 10%; rms Current Density = 20×10^{-6} A cm^{-2}; Frequency = 50 Hz.

(a) Titration of 10 ml of 0.01 M Thymol with 0.1 M Bromine; (b) Titration of 10 ml of 0.01 M Hydroquinone with 0.1 M Bromine; (c) Titration of 10 ml of 0.01 M Thymol with 0.1 M Bromine in the Presence of Three Equivalents of Pyridine; (d) Titration of 10 ml of 0.01 M Diphenylamine with 0.1 M Bromine; (e) Titration of 10 ml of 0.01 M Benzidine with 0.1 M Bromine; (f) Titration of 10 ml of 0.01 M Oleic Acid with 0.1 M Bromine; (g) Titration of 10 ml of 0.01 M Methyl Linoleate with 0.1 M Bromine.

represent the end-points. The ratio between thymol and bromine was found to be 1:3 and that of hydroquinone and bromine was 1:4.

The addition of pyridine to thymol and/or hydroquinone in a 3:1 mole ratio [6] was found to only have a slight effect on the bromination reaction. This is obvious from the small improvement that has resulted in the titration curve of thymol which indicates that the reaction of bromine with thymol is still slow even in the presence of pyridine (Figure 1c). This titration was repeated three times, but we were unable to confirm the results of Kratochvil and others [6] who have reported that the reactions of phenols with bromine are rapid in the presence of pyridine. They considered pyridine to be a strong base in PC, catalyzing the bromination of phenols by enhancing the release of the replaceable protons. However, it might be expected that the basic strength of pyridine would be suppressed in PC, an aprotic solvent having basic properties [8]. Therefore, it is more reasonable to expect that pyridine may have only a slight catalytic effect on the bromination of certain phenols in PC. This effect can be attributed to the electrophilic attack of a pyridine–bromine complex [5] rather than to the unlikely basic behavior of pyridine in PC.

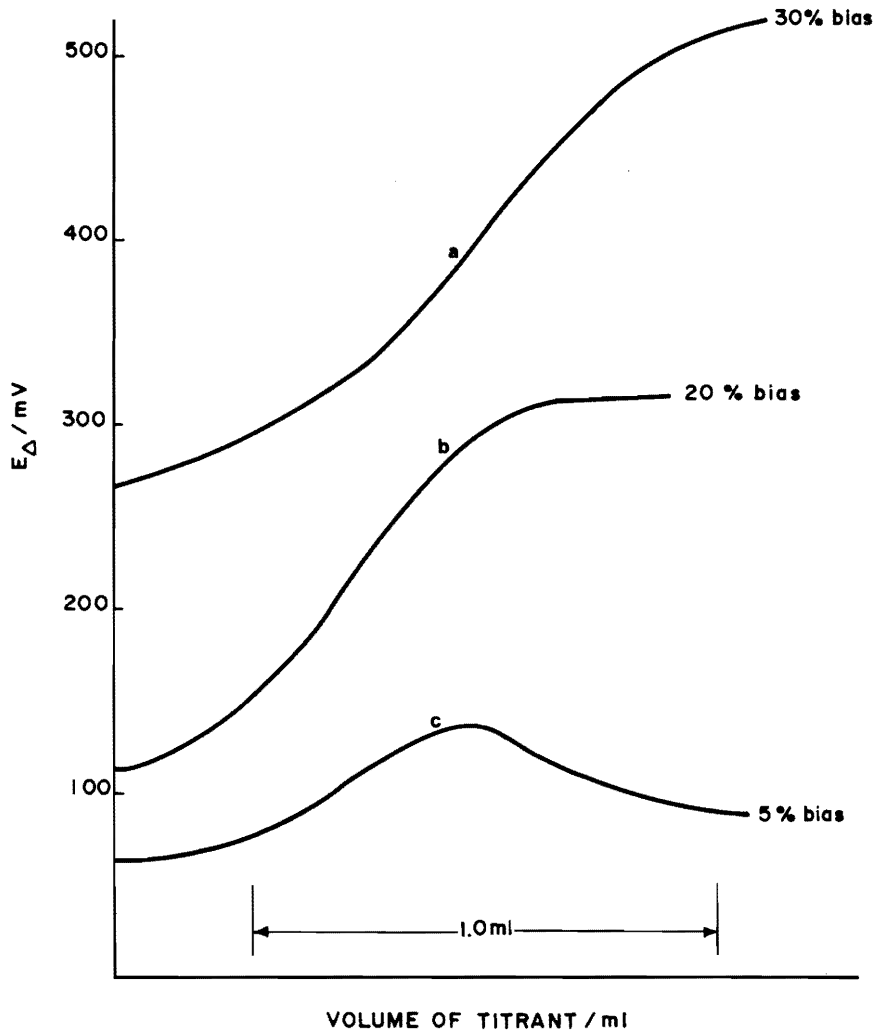

Figure 2. Msb Differential Curves of L-ascorbic Acid.
(a) Titration of 10 ml of 0.01 M L-ascorbic Acid with 0.1 M Bromine at 30% Bias. The rms Current Density $= 43 \times 10^{-6}$ *A cm*$^{-2}$; *(b) At 20% Bias and rms Current Density of* 30×10^{-6} *A cm*$^{-2}$; *(c) At 5% Bias and rms Current Density of* 10×10^{-6} *A cm*$^{-2}$.

It has been reported that aromatic amines can also be titrated directly with bromine in PC [6]. Compounds like aniline and *p*-toluidine have been considered to be basic in PC and they were titrated directly with bromine. During this work, the direct titration of aniline was attempted, but this time the results of Kratochvil and others [6] could not be confirmed because the reaction of aniline with bromine was found to be very slow.

The slow bromination of phenols and aromatic amines in propylene carbonate can be attributed to the following reasons. First, the three positions in phenol as well as in the aromatic amine ring undergo bromination at different rates. For instance, the bromination of one of the *ortho* positions in the phenol ring can be fast, but the other positions need more time to be brominated. Second, the solvent used is an aprotic one and it does not enhance the release of the replaceable proton. Hence, the bromination process will be retarded.

Diphenylamine and benzidine are colorless indicators which are oxidized to deeply colored di-cation radicals via a two-electron step [9]. The direct titration of these compounds with bromine was performed in PC. The titration curves obtained are shown in Figure 1 (d and e). It can be seen from these curves that the reactions of diphenylamine and benzidine are also slow in PC. Each of these titrations was found to last for 2 hours. However, it is interesting to note that these reactions do not show any change in color, but

that a white precipitate is formed in each case. The ratio of diphenylamine to bromine was found to be 1:4 and that of benzidine to bromine was 1:2. These ratios are similar to those obtained in anhydrous acetic acid and have been considered to correspond to nuclear bromination [3].

Bromine values for certain fatty acids and their methyl esters have been determined in PC by direct titration with bromine [9]. It has been reported that the potentiometric titration of a fatty acid such as oleic acid takes only 5–6 minutes [9]. Based on this published work, the direct titrations of oleic acid and methyl linoleate were attempted in a mixture of 2:1 PC-chloroform [7] and were expected to be fast. However, each titration was found to require more than two hours for completion. The titration curves obtained are shown in Figure 1 (f for oleic acid and g for methyl linoleate). It is evident from these curves that bromine adds slowly to the double bonds in these compounds. Hence, their direct titration with bromine in PC is difficult.

The direct titration of L-ascorbic acid was done initially at 30% bias [1]. The resulting titration curve (Figure 2a) shows a high overvoltage which is probably due to the high current density that was employed. A similar titration curve was also obtained, but with less overvoltage, when the percent bias was decreased to 20% (Figure 2b). It is clear that these curves are of no value for the location of the end-point. However, on decreasing the percentage bias to 5%, a broad asymmetric curve was obtained indicative of the slow oxidation of L-ascorbic acid in PC. Although the titration is slow and lasts for about one hour, the end-point can be easily located by extrapolating the straight sides of the curve. The point of intersection represents the end-point.

CONCLUSION

The applicability of msb DEP to substitution and oxidation reactions in PC was examined. In contrast to previous results, the direct titration of phenols amines and olefins was found to be difficult because of the slow reactions with bromine even in the presence of pyridine. The oxidation of L-Ascorbic acid was also found to be slow in PC.

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