

## Electrochemical Oxidation of Fragrances 4-Allyl and 4-Propenylbenzenes on Platinum and Carbon Paste Electrodes

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**Abstract.** The electrochemical oxidation behaviors of 4-allylbenzenes (estragole, safrole and eugenol) and 4-propenylbenzenes (anethole, asarone and isoeugenol) on platinum and carbon paste electrodes were investigated in a Britton-Robinson buffer (pH = 2.93 and 10.93), acetate buffer, phosphate buffer solutions (pH = 2.19 and 6.67), and acetonitrile containing various supporting electrolytes examined lithium perchlorate. Their oxidation potential with Hammett (free-energy relationships) and possible reaction mechanisms were discussed.

**Keywords:** electrochemical oxidation, 4-allylbenzenes, 4-propenylbenzenes

### INTRODUCTION

Research on fragrances / flavors is popular; however, almost all studies focus on their wide application in the food, and cosmetics industries and in traditional medicine; as well as extraction methods and analytical methodologies.<sup>1–5</sup> Fragrances that are air-sensitive may form peroxides, respiratory irritants, and aerosol particles that cause inflammatory responses in the lungs. The photochemistry of some allylic compounds such as cis-trans isoeugenol and citral, were oxidized in the presence of atmospheric oxygen or photosensitized species (O<sub>3</sub>, OH, NO<sub>3</sub>, etc.).<sup>6–8</sup> However, most reports have focused on the photochemical reaction of eugenol derivatives to for the synthesis of new flavors chemicals.<sup>9–14</sup> The structurally related substituted 4-allylbenzenes derivatives (eugenol, estragole and safrole) and 4-propenylbenzenes derivatives (isoeugenol, anethole and asarone), occur naturally in various traditional foods, particularly in spices such as cloves, cinnamon and basil. Some of them have been demonstrated to be an effective, inexpensive anesthetic agents, antioxidants and blood circulation enhancers. The major analytical methods for analyzing alkenylbenzenes fragrances are gas chromatography and gas chromatography-mass spectrometry.<sup>15</sup> There are few electrochemical theories reported in pharmaceutical formulations.<sup>16</sup> 4-allylbenzenes (4-allylanisole and eugenol) and 4-propenylbenzenes (*trans*-anethole) are

studied to undergo electrochemical polymerization giving rise to either conducting or insulating films.<sup>17–19</sup> The anodic methoxylation of alkenylbenzenes includes anethole and isosafrole on graphite and platinum, which can be converted to free aldehyde, a valuable fragrance compound and an intermediate for organic synthesis.<sup>20–23</sup> The present work is concerned with the measurement of aromatic substituent effects and structural elucidation of 4-allyl and 4-propenylbenzenes.

### EXPERIMENTAL

#### Apparatus and Materials

Voltammetric measurements were performed using an EG&G Princeton Applied Research Model 394 Polarographic Analyzer (Princeton, NJ, USA) and potentiostat/galvanostat (263A; EG&G Princeton Applied Research, Princeton, NJ, USA). The absorption spectra of fragrances were determined using a spectrophotometer (2000/IRDM FTIR; Perkin-Elmer, Fremont, CA, USA) with an attenuated total reflection (ATR) system (Gateway ATR; SpecacInc., Smyrna, GA (now Cranston, RI), USA). The Raman spectra were recorded using a micro-Raman setup (JASCO NR-1000; Sunway Scientific Corporation, Taipei, Taiwan). The spectrometer had a focal length of 300 nm and was equipped with a dispersive element 1800 lines/mm grating, resulting in a resolution of 1.2 cm<sup>-1</sup>.

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Pure standard substances were purchased from biomedical supply houses: eugenol, isoeugenol, and *trans*-anethole from Acros Organics, Geel, Belgium;  $\alpha$ -asarone, safrole from Sigma-Aldrich Fine Chemicals, Fluka, Switzerland; estragole from Aldrich Chemical Company, Inc., Milwaukee, WI. Supporting electrolytes were obtained as follows: tetrabutylammonium tetrafluoroborate ( $\text{Bu}_4\text{NBF}_4$ , Acros Organics, Thermo Fisher Scientific, Geel, Belgium), tetraethylammonium tetrafluoroborate ( $\text{Et}_4\text{NBF}_4$ , E. Merck, Chemical Co. Germany), tetrabutylammonium perchlorate ( $\text{Bu}_4\text{NClO}_4$ , Tokyo Chemical Industry Co., Ltd, Tokyo, Japan), tetraethylammonium perchlorate ( $\text{Et}_4\text{NClO}_4$ , Tokyo Chemical Industry Co., Ltd, Tokyo, Japan), and lithium perchlorate ( $\text{LiClO}_4$ , Acros Organics, Thermo Fisher Scientific, Geel, Belgium). Other chemical reagents used were of analytical grade.

### Voltammetric Measurements

The three voltammetric techniques, Sampling DC, linear Sweep and cyclic voltammetry, were all performed on a platinum and carbon paste electrodes. Cyclic voltammograms (CV) of the fragrances were taken on a platinum electrode in acetonitrile containing various supporting electrolytes, and Britton-Robinson buffer solutions (pH = 2.93 – 10.93) to monitor potential *vs.* current.

## RESULTS AND DISCUSSION

### Electrochemical Behavior of Fragrances 4-Allyl and 4-Propenylbenzenes on the Platinum Electrode

#### *Supporting Electrolytes and Solvent Effects*

There are several ways in which the supporting electrolytes solvent system can influence mass transfer, the electron reaction (electron transfer), and the chemical reactions which are coupled to the electron transfer.<sup>24</sup> The effects of supporting electrolytes and solvent composition on fragrances 4-allyl and 4-propenylbenzenes peak potential ( $E_p$ ) and peak current ( $i_p$ ) are listed in Table 1. Table 1 shows the peak current of fragrances in non-aqueous solvent (100 % acetonitrile) were higher than in aqueous-organic solvent (30 % acetonitrile) due to the higher background in non-aqueous solvent than that in aqueous-organic solvent. However, the peak potential of fragrances were less positive in aqueous organic solvents that are more suitable for oxidation. The electrooxidation process occurs in the heterogeneous phase. For non-aqueous solvent, its molecules completely cover the electrode surface to prevent the adsorption of fragrances. Furthermore in organic work, strongly basic anions or radical anions are often produced and these are rapidly protonated by solvents like

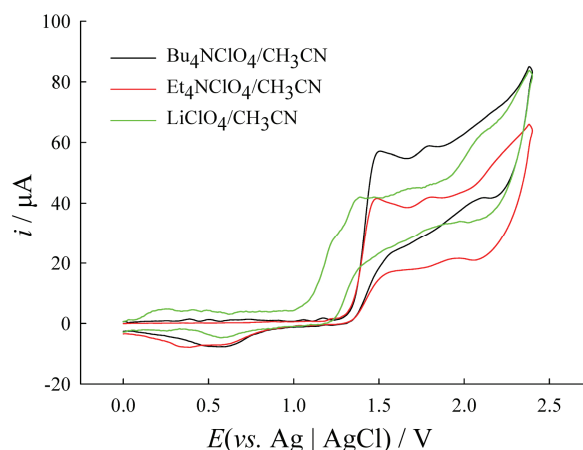
**Table 1.** Effect of supporting electrolytes on the cyclic voltammetric peak potential ( $E_p$ ) and peak current ( $i_p$ ) of  $\alpha$ -asarone, *trans*-anethole, isoeugenol, safrole, estragole and eugenol at platinum electrode. The concentration of fragrances was 1 mmol dm<sup>-3</sup>; scan rate,  $\nu$  = 50 mV/s.

	$\alpha$ -Asarone		<i>trans</i> -Anethole		Isoeugenol		Safrole		Estragole		Eugenol	
	$E_p$ /V	$i_p$ / $\mu$ A	$E_p$ /V	$i_p$ / $\mu$ A	$E_p$ /V	$i_p$ / $\mu$ A	$E_p$ /V	$i_p$ / $\mu$ A	$E_p$ /V	$i_p$ / $\mu$ A	$E_p$ /V	$i_p$ / $\mu$ A
$\text{Bu}_4\text{NBF}_4/\text{CH}_3\text{CN}$	0.91	20.6	1.33	35.7	0.84	24.4	1.57	62.0	1.67	80.1	1.17	44.9
	1.19	36.2	1.78	72.9	1.18	54.5	1.78	62.6	2.12	98.2	— <sup>(a)</sup>	— <sup>(a)</sup>
	1.44	34.6	2.14	136	1.42	94.5	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>
$\text{Et}_4\text{NBF}_4/\text{CH}_3\text{CN}$	0.99	30.3	1.31	28.8	1.10	26.2	1.51	41.6	1.67	61.3	1.23	35.1
	1.31	28.8	1.68	46.9	1.25	38.9	1.88	84.6	2.13	75.1	— <sup>(a)</sup>	— <sup>(a)</sup>
	1.86	45.9	2.11	98.0	1.52	45.8	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>
$\text{Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}$	1.20	31.6	1.26	49.2	1.10	29.0	1.51	57.2	1.67	54.9	1.27	41.0
	1.43	37.6	1.65	69.6	1.27	41.5	1.80	58.9	2.06	82.5	— <sup>(a)</sup>	— <sup>(a)</sup>
	1.71	49.0	2.06	150	1.51	42.4	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>
$\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$	1.15	35.5	1.32	34.2	1.08	28.5	1.49	41.7	1.64	69.7	1.18	41.7
	1.40	41.4	1.67	51.0	1.27	44.7	1.81	42.1	2.13	83.7	— <sup>(a)</sup>	— <sup>(a)</sup>
	1.72	49.8	2.11	115	1.48	49.0	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>
$\text{LiClO}_4/\text{CH}_3\text{CN}$	1.13	32.8	1.25	32.8	1.00	27.6	1.39	42.2	1.61	51.1	1.16	42.2
	1.36	33.3	1.60	59.6	1.18	45.4	2.09	62.7	2.07	7.81	— <sup>(a)</sup>	— <sup>(a)</sup>
	1.73	37.9	2.00	114	1.43	55.3	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>
$\text{Et}_4\text{NBF}_4/\text{CH}_3\text{CN}$ , $w(\text{CH}_3\text{CN}) = 30\%$	0.76	12.7	1.11	24.2	0.61	9.81	1.18	47.3	1.37	42.0	0.85	23.7
	0.99	21.7	1.57	67.17	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>
$\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$ , $w(\text{CH}_3\text{CN}) = 30\%$	0.76	11.0	1.00	20.9	0.64	9.00	1.17	51.8	1.37	48.9	0.83	18.9
	0.97	17.1	1.58	69.04	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>
$\text{LiClO}_4/\text{CH}_3\text{CN}$ , $w(\text{CH}_3\text{CN}) = 30\%$	0.76	12.9	1.11	20.8	0.69	9.56	1.19	48.8	1.38	56.1	0.92	17.8
	0.97	21.1	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>	— <sup>(a)</sup>

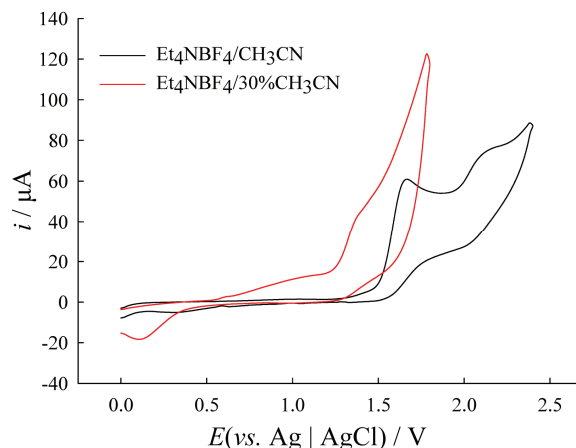
<sup>(a)</sup> Not determined

water or alcohol. These reasons explain why aqueous organic solvents are more suitable for the oxidation of the allyl and propenylbenzenes. The solubilities and specific resistance of  $\text{Bu}_4\text{NBF}_4/\text{CH}_3\text{CN}$  ( $s = 70 \text{ g}/100 \text{ ml}$ ,  $\rho = 37 \ \Omega \text{ m}$ ) and  $\text{Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}$  ( $s = 71 \text{ g}/100 \text{ ml}$ ,  $\rho = 31 \ \Omega \text{ m}$ ) are very near. Therefore, the  $E_p$  and  $i_p$  of the fragrances are very similar.

The cation of the supporting electrolytes significantly influencing the safrole, estragole and eugenol on  $E_p$  and  $i_p$  is confirmed by the results listed in Table 1. From Table 1, it is 1.51 V for  $\text{Bu}_4\text{NClO}_4$  and 1.49 V for  $\text{Et}_4\text{NClO}_4$  but the  $i_p$  in  $\text{CH}_3\text{CN}$  containing  $\text{Bu}_4\text{NClO}_4$  (57.2  $\mu\text{A}$ ) is 1.4 times that of in  $\text{Et}_4\text{NClO}_4$  (41.7  $\mu\text{A}$ ). These results can be accounted for by the presence of larger ion tetrabutylammonium than the tetraethylammonium film on the platinum surface. However, the  $E_p$  of quaternary ammonium ion film on the Pt surface is very similar. Compared with quaternary ammonium ion and  $(\text{R}_4\text{N}^+)$  lithium ion ( $\text{Li}^+$ ), the  $E_p$  of the safrole in  $\text{Bu}_4\text{NClO}_4$ ,  $\text{Et}_4\text{NClO}_4$  and  $\text{LiClO}_4$ , small cation size of lithium ion show less positive values (1.39 V) than quaternary ammonium ion (1.57 V) (Figure 1). Indeed, as reported in the literature,<sup>25</sup> the bulky hydrophobic alkyl group stronger Van der Waals forces of cohesion between the ammonium groups, leading to a more compact hydrophobic adsorbed layer. The  $E_p$  of the estragole first peaks are expected to correspond to the processes of two a one-electron ( $E_p$  at 1.67 V and 2.13 V) and a one two-electron ( $E_p$  at 1.37 V) oxidation, in non-aqueous solvent (acetonitrile) and aqueous-organic solvent (30 % acetonitrile) (Figure 2). These data show the peak potentials shift more positively with 100 % acetonitrile, because its molecules completely cover the electrode surface to prevent the adsorption of estragole. However, 30 % acetonitrile point to an appreciable content of estragole adsorbed on the electrode surface.<sup>26</sup>

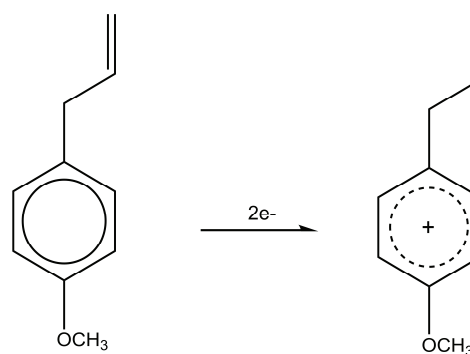


**Figure 1.** The effect of solvent (acetonitrile) containing various supporting electrolytes on the cyclic voltammograms of safrole at platinum electrode. Supporting electrolytes: tetrabutylammonium perchlorate ( $\text{Bu}_4\text{NClO}_4$ ); tetraethylammonium perchlorate ( $\text{Et}_4\text{NClO}_4$ ); lithium perchlorate ( $\text{LiClO}_4$ ).



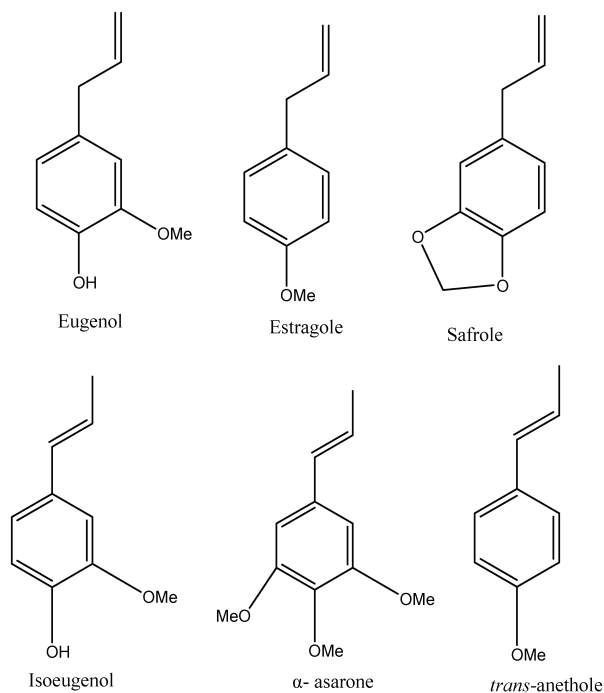
**Figure 2.** The effect of nonaqueous aprotic solvent (acetonitrile) and 30 % acetonitrile containing  $\text{Et}_4\text{NBF}_4$  on the cyclic voltammograms of estragole at platinum electrode.

The total number of electrons is determined using controlled-potential coulometry using a platinum electrode. The accumulated charge ( $Q$ ) is taken from the digital coulometer at a curve (potential corresponding to peak current) of the oxidation wave. Applying the equation:  $Q = nFw/M$  where  $w$  is the weight of the sample in grams and  $M$  its molecular weight, the value of  $n$  for estragole is found to be two electrons.<sup>19,27</sup> The active oxidation group (OH) on benzene ring of estragole because of between C=C double bond and benzene ring has not conjugation results a marked higher potential (1.61 V) than that has conjugation of trans-anethole (1.25 V) in acetonitrile containing  $\text{LiClO}_4$ . A possible mechanism is given as below:



#### Substituted Group Effects

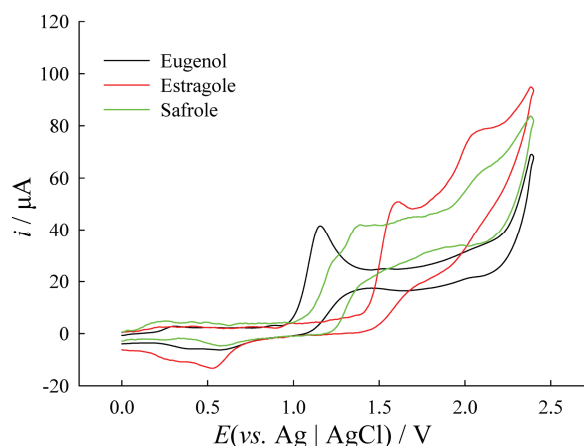
Insofar as electrons are transferred in the potential-determining step, the transition state is more electron rich than the reactant is, and electron-donating substituents will facilitate to oxidation process.<sup>28</sup> Voltammetric oxidative groups (*i.e.* hydroxyl and methoxyl) are electron-donating substituents these attached to the 4-allylbenzene nucleus and 4-propenylbenzenes (structure shown in Scheme 1) will affect the electronic distribution within that nucleus. The substituents constant values can be quantitatively divided into the sum of



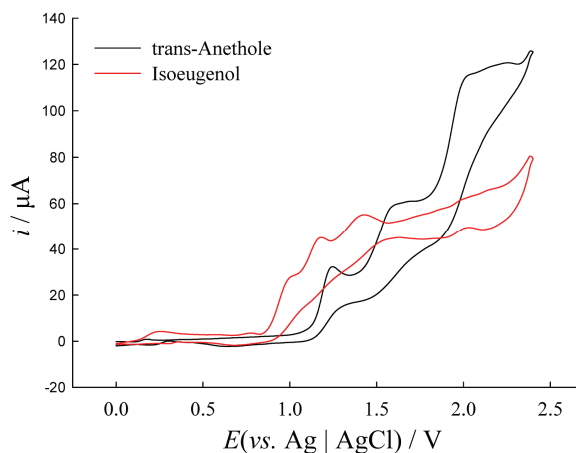
**Scheme 1.** The fragrance structure of eugenol, estragole, safrole, isoeugenol,  $\alpha$ -asarone, and *trans*-anethole.

independent inductive and resonance contributions.<sup>29</sup> The following peak potentials are reported for substituted 4-allylbenzenes in  $\text{LiClO}_4/\text{CH}_3\text{CN}$  ( $w(\text{CH}_3\text{CN}) = 100\%$ ): hydroxyl +1.16 V, methoxyl +1.64 V and methylenedioxy +1.49 V. (Figure 3) Eugenol is oxidized more easily than the estragole and safrole. The same substituents at 4-propenylbenzenes have resonance effect because involves interaction between double bond and benzene ring, and give three peaks. Figure 4 demonstrates the effect of the hydroxyl and methoxyl substituents on the oxidation of isoeugenol and *trans*-anethole and both have three peaks.

The vibrational spectroscopic features of fragrances demonstrate the relationship between substituents and

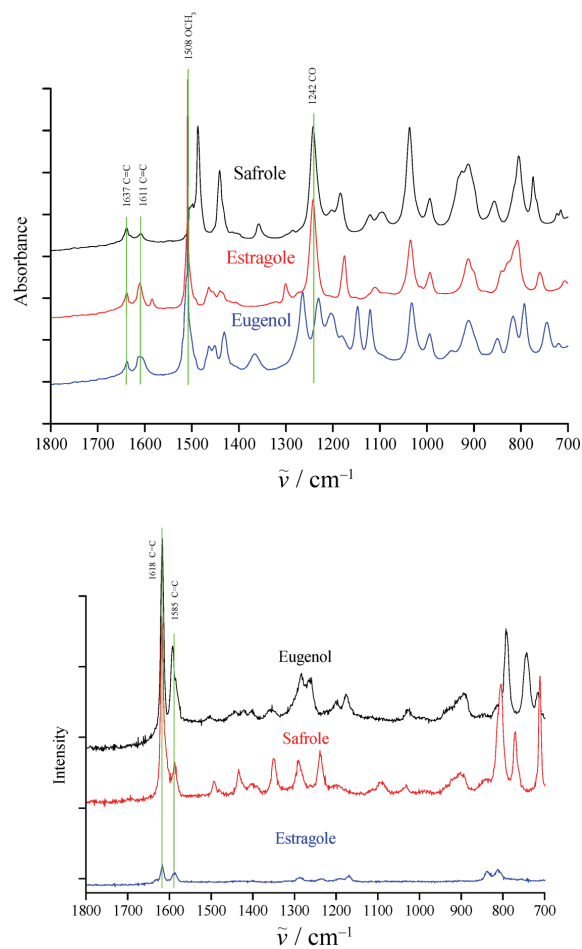


**Figure 3.** The effect of substituted 4-allylbenzenes at platinum electrode in nonaqueous aprotic solvent (acetonitrile) containing lithium perchlorate ( $\text{LiClO}_4/100\%\text{CH}_3\text{CN}$ ).



**Figure 4.** The effect of substituted 4-propenylbenzenes at platinum electrode in nonaqueous aprotic solvent (acetonitrile) containing lithium perchlorate ( $\text{LiClO}_4/100\%\text{CH}_3\text{CN}$ ).

vinyl double bond. Both ATR-IR and Raman have  $\text{C}=\text{C}$  aromatic and conjugate bands about  $1600\text{ cm}^{-1}$  (Figure 5(a) and (b)). The ATR-IR spectra of 4-allylbenzenes (safrole, estragole and eugenol) have



**Figure 5.** (a) ATR-IR spectroscopy for structure of 4-allylbenzenes (safrole, estragole and eugenol) (b) Raman spectroscopy for structure of 4-allylbenzenes (safrole, estragole and eugenol)

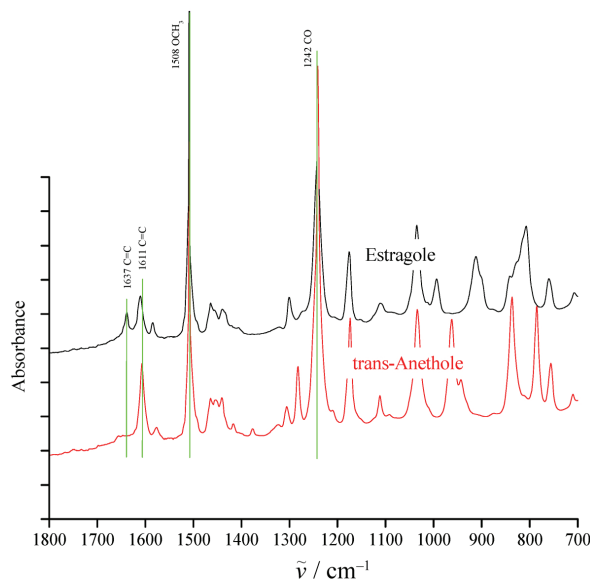
highly similar characteristics because of the presence of the same weak bands  $1611\text{ cm}^{-1}$  for  $\nu(\text{C}=\text{C})_{ar}$  and  $1637\text{ cm}^{-1}$  for  $\nu(\text{C}=\text{C})_{vin}$ , strong band  $1508\text{ cm}^{-1}$  for  $\nu(-\text{OCH}_3)$  in estragole and eugenol, and strong band  $1242\text{ cm}^{-1}$  for  $\nu(\text{C}-\text{O})$ . On the other hand, the Raman spectra of these compounds show quite similar strong bands at  $1584\text{ cm}^{-1}$  for  $\nu(\text{C}=\text{C})_{ar}$  and  $1618\text{ cm}^{-1}$  for  $\nu(\text{C}=\text{C})_{vin}$ . However, from Figure 6 shows  $1637\text{ cm}^{-1}$  for  $\nu(\text{C}=\text{C})_{vin}$  in trans-anethole is not apparent because of the resonance effect between the double bond and the benzene ring.

### Fragrances on the Platinum and Carbon Paste Electrodes

#### pH Effects

The  $E_p$  and  $i_l$  in the Sampling DC voltammetric oxidation over a wide pH range are found to substantially vary from each other. The  $E_p$  and  $i_l$  obtained in the present work on the platinum and carbon electrodes are listed in Table 2. Notes, the  $E_p$  decreasing with an increasing pH does not obviously change in weak acidic media (pH = 2.93–5.39), but significantly decreased above pH = 6.14. Safrole and estragole differing from the other fragrances have two peaks above pH = 6.14 in alkaline media. However, there are two discrepancies between the voltammetric behaviors on the platinum (Pt) and carbon paste electrodes (CPE): (1) A higher value of limiting current ( $i_l$ ) in strong acidic media (pH = 2.93–3.89) at CPE; but higher  $i_l$  in weak acidic media (pH = 6.18–6.83) at Pt; (2)  $E_p$  decreasing with an increasing pH at Pt is clearly more regular than that CPE. Our analyses of the effect of pH and supporting electrolytes on the oxidation peak current and peak potential of fragrances in acidic solutions (pH = 2.19–6.83) and in the electrolyte of lithium perchlorate (pH = 6.04) showed the peaks shifted to a less to positive potential in acetate buffer and that the peak current in phosphate buffer (pH = 2.19) was higher than in the others (Figure 7). This indicates the oxidation of fragrances is strongly pH-dependent. The  $E_p - E_{p/2}$  ( $E_{p/2}$  = half-peak potential) values in pH = 2.93–8.81 at Pt and CPE electrodes are shown in Table 3.  $E_p - E_{p/2}$  gave a range of 90–190 mV and 80–170 mV in acidic media at the Pt and CPE electrodes respectively. For a reversible charge transfer, the  $E_p - E_{p/2}$  should be around 60 mV ( $E_p - E_{p/2} = 47.7\text{ mV}/\alpha n_a$  at 298 K). Hence, it may be concluded the mechanism for the oxidation of fragrance is an irreversible charge transfer at both Pt and CPE electrodes in acidic media. At a pH below 6.14, only one-electron peak was observed since the second one-electron step is obscured by hydrogen evolution. The  $\alpha$ -Asarone and eugenol undergoes oxidation in two steps (two one-electron), which are observed at pH above 6.83 and shown in Table 3.

The effect scan rate on the electrooxidation of isoeugenol was examined in pH = 6.14 in the range of



**Figure 6.** ATR-IR difference spectroscopy for structure of 4-allylbenzene (estragole) And 4-propenylbenzene (trans-Anethole)

10 mV/s to 800 mV/s. In this case the oxidative peak current was proportional to the square root of the scan rate on Pt and CPE electrodes, respectively. From Figure 8 A, good linearity of the regression equation being  $y = 11.4x + 70.3$ , the correlation coefficient  $r = 0.9900$  for Pt electrode;  $y = 2.45x - 5.27$ , the correlation coefficient  $r = 0.9961$  for CPE. Under these conditions the currents were diffusion controlled. The relationship between peak potential and the logarithm of the scan rate (Figure 8(b),  $y = 0.14x + 0.39$ , the correlation coefficient  $r = 0.9906$  for Pt electrode;  $y = 0.13x + 0.55$ , the correlation coefficient  $r = 0.9950$  for CPE) can be used to roughly estimate the number of electrons involved in the catalytic oxidation.

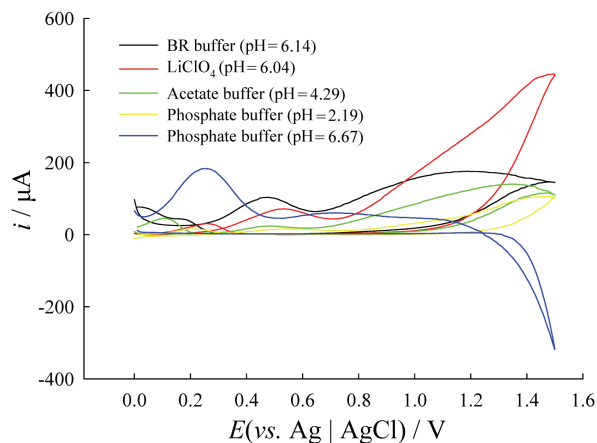
#### Structure and Reactivity

The two linear portions [plotted for  $(\text{p}K-1) > \text{pH} > (\text{p}K+1)$ ] intersect at a pH value corresponding to pK. The  $E_{1/2}$  and pH values were input into the computer and using the simple regression method of the regression analysis the best two equations were found. These were solved to find the pK values. The  $E_{1/2}$  vs. pH plot of  $\alpha$ -asarone on Pt (pK = 4.60) and CPE (pK = 4.88) electrodes were given in Figure 9. By using the substituent constant ( $\delta_H$ ) value of trans-anethole as 0, the other substituent constants ( $\delta_x$ ) of fragrances calculated from  $\text{p}K_H - \text{p}K_x$  are  $-0.30$ ,  $-0.40$ ,  $-0.57$ ,  $-2.0$ ,  $-1.0$ , for eugenol,  $\alpha$ -asarone, safrole, estragole, and isoeugenol, respectively. Most of the data may be correlated by a modified Hammett equation,  $E_{1/2} = \rho\delta_x$ ,  $\rho(-1.15)$  is a voltammetric reaction constant. The Hammett  $\delta$ - $\rho$  linear free-energy relationship is useful for evaluating substituent effects in a system. The rate of oxidation is greatly increased by the electron-donating substituent ( $-\text{OH}$  and  $-\text{OMe}$ ).

**Table 2.** Comparative Sample DC voltammetric behavior – peak potential ( $E_p$ ) and peak current ( $i_p$ ) – of fragrances in Britton and Robinson buffer on platinum and carbon paste electrodes (CPE)

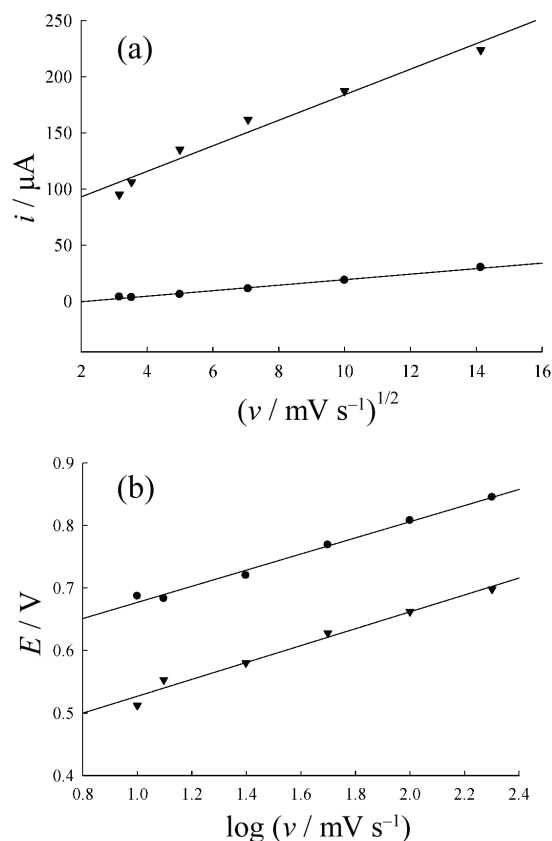
pH	$\alpha$ -Asarone				trans-Anethole				Isoeugenol				Safrole				Estragole				Eugenol									
	$E_p/V$	$i_p/\mu A$	CPE	Pt	$E_p/V$	$i_p/\mu A$	CPE	Pt	$E_p/V$	$i_p/\mu A$	CPE	Pt	$E_p/V$	$i_p/\mu A$	CPE	Pt	$E_p/V$	$i_p/\mu A$	CPE	Pt	$E_p/V$	$i_p/\mu A$	CPE	Pt	$E_p/V$	$i_p/\mu A$	CPE	Pt		
2.93	0,49	-43	0,59	-106	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	0,38	-7,82	0,31	-64,5	0,87	-36,7	0,76	-24,31	1,09	-89,3	0,85	-36,7	0,47	-11,8	0,35	-75,3							
3.89	0,45	-33,4	0,6	-90	0,4	-18,2	0,77	-1,92	0,32	-7,59	0,31	-62,3	0,86	-24,1	0,67	-24,2	1,12	-104	0,91	-13,4	0,44	-11,1	0,36	-54						
4.46	0,48	-51,2	0,6	-84,8	0,38	-36,7	0,77	-0,13	0,32	-12,2	0,27	-14,7	0,89	-41,6	0,66	-9,34	1,1	-67,3	0,94	-30,6	0,45	-5,55	0,3	-45,4						
5.39	0,29	-24,6	0,57	-46,6	0,32	-53,6	0,94	0,3	0,3	-15	0,38	-13,5	0,84	-47,5	0,63	-17,2	0,9	-44,3	0,58	-6,94	0,38	-4,12	0,35	-46,1						
6.14	0,26	-20,7	0,48	-48,9	0,33	-65,7	0,56	0,28	0,3	-91	0,35	-19,5	0,9	-31,6	0,62	-9,98	0,91	-57,7	- <sup>(a)</sup>	- <sup>(a)</sup>	0,34	-65,6	0,3	-53,9						
6.83	0,22	-47,1	0,28	-15,9	0,32	-91	0,53	-0,73	0,22	-69,5	0,32	-13,9	0,9	-32,1	0,58	-15,5	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	0,26	-31	0,3	-55,1						
7.46	0,76	-44,2	0,55	-39,9	0,95	-138	0,91	-0,23	0,8	-56,1	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	0,74	-40,7									
8.27	0,53	-17,4	0,44	-70,3	0,37	-88,7	0,72	2,15	- <sup>(a)</sup>	- <sup>(a)</sup>	0,29	-15,4	0,91	-13,4	0,56	-18,5	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	0,25	-27,3	0,22	-51,8							
	0,84	-13,9	0,78	-67	0,91	-118	1,02	4,94												0,65	-33,2	0,55	-34,6							
	0,6	-5,19	0,65	-45,4	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	0,93	-11,7	0,54	-6,91	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	- <sup>(a)</sup>	0,2	-46,4								
	0,8	-9,12	0,77	-49																	0,52	-28,1								
	1,11	-15,7																												

<sup>(a)</sup>Not determined



**Figure 7.** The effect of pH on the voltammograms for  $9.09 \times 10^{-4}$  M of *trans*-anethole on platinum electrode and scan rate 50 mV/s. Britton-Robinson buffer solution (pH = 6.14, black line); LiClO<sub>4</sub> (pH = 6.04, red line); acetate buffer (pH = 4.29, green line); phosphate (pH = 2.09, yellow line); phosphate (pH = 6.67, blue line).

The positive potential order is estragole > safrole > eugenol due to the –OH strongly activating group than –OMe in the para-position. However, the overall rate enhancement arises from a sum of the groups' inductive and resonance effects. Therefore, 4-propenylbenzenes (isoeugenol,  $\alpha$ -asarone, and *trans*-anethole) have both inductive and resonance effects. The same substituents in the 4-allyl (eugenol) and 4-propenylbenzenes (isoeugenol), when there is isoeugenol through-resonance between a reaction site that becomes electron-rich. Thus, the potential of isoeugenol shifts is less positive



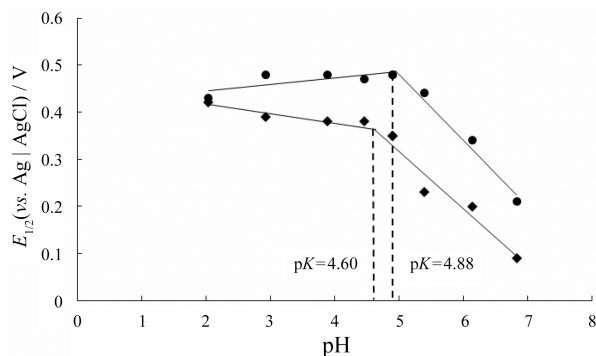
**Figure 8.** Magnitude of the peak current for isoeugenol oxidation as a function of square root of scan rate on Pt ( $\blacktriangledown$ ) and CPE ( $\bullet$ ) electrodes (a); and peak potentials of isoeugenol oxidation as a function of logarithm of scan rates on Pt ( $\blacktriangledown$ ) and CPE ( $\bullet$ ) electrodes (b).

**Table 3.** Comparative linear sweep voltammetric behavior of fragrances in Britton-Robinson buffer on platinum (Pt) and carbon paste electrodes (CPE) where  $E_p$  is peak potential, and  $E_{p/2}$  is half-peak potential

pH	$\alpha$ -Asarone		Eugenol	
	Pt	CPE	Pt	CPE
	$(E_p - E_{p/2}) / \text{mV}$	$(E_p - E_{p/2}) / \text{mV}$	$(E_p - E_{p/2}) / \text{mV}$	$(E_p - E_{p/2}) / \text{mV}$
2.93	180	180	100	90
3.89	190	190	100	90
4.46	170	190	100	80
5.39	140	190	100	80
6.14	90	160	170	100
6.83	120	140	130	80
	170	100	170	– <sup>(a)</sup>
7.46	50	100	140	80
	40	100	160	– <sup>(a)</sup>
8.27	70	50	– <sup>(a)</sup>	80
	60	160	– <sup>(a)</sup>	– <sup>(a)</sup>
8.81	70	70	– <sup>(a)</sup>	– <sup>(a)</sup>
	60	120	– <sup>(a)</sup>	– <sup>(a)</sup>

<sup>(a)</sup> Not determined





**Figure 9.** The relations of  $E_{1/2}$  and pH of  $\alpha$ -Asarone on Pt (♦) and CPE (●) electrodes.

than that of eugenol. The same as substituents of *trans*-anethole and estragole in the benzene, likewise the potential of *trans*-anethole shifts less positively than that estragole.

## CONCLUSION

The fragrances of the ally and propenyl derivatives of phenol and phenol ethers have similar of the irreversible oxidation potentials, and their potential is closely dependent on the structural factors. Thus, compared with various electron-donating groups and conjugation results on platinum and carbon paste electrodes.

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