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Cyclic Voltammetric Characteristics of Tri- and Diarylcarbenium Salts Having Some Methoxyphenyl Groups

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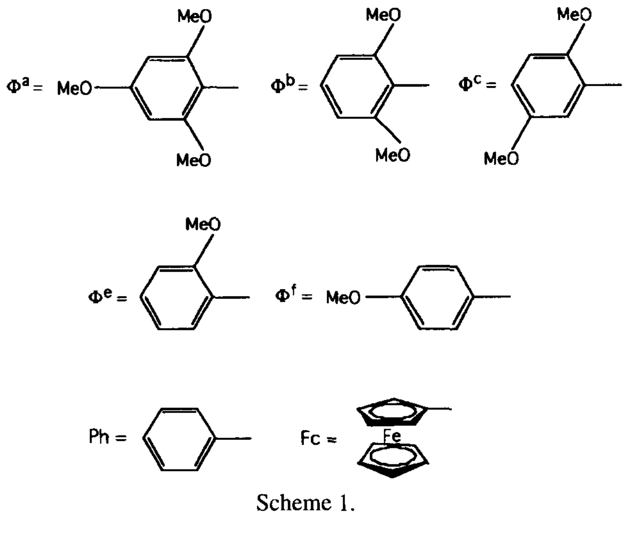
Triarylcarbenium salts ($\Phi^a{}_3C^+$, $\Phi^a\Phi^b{}_2C^+$, $\Phi^b{}_3C^+$, $\Phi^f\Phi^b{}_2C^+$, $\Phi^e\Phi^b{}_2C^+$, $Ph\Phi^b{}_2C^+$, and $FcC^+\Phi^bPh$ [Φ^a, Φ^b, Φ^e, Φ^f, Ph, Fc = 2,4,6-$(MeO)_3C_6H_2$, 2,6-$(MeO)_2C_6H_3$, 2-$(MeO)C_6H_4$, 4-$(MeO)C_6H_4$, C_6H_5, $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)$]) showed a reversible redox wave with one-electron transfer at a Pt electrode in 1,2-dichloroethane, while the reduction of diarylcarbenium salts ($\Phi^a{}_2C^+H$, $FcC^+\Phi^aH$, $FcC^+\Phi^bH$, $FcC^+\Phi^cH$, $FcC^+\Phi^eH$, and FcC^+PhH [Φ^c = 2,5-$(MeO)_2C_6H_3$]) proceeded irreversibly. A wide range of cathodic shifts in the redox potentials (198—−377 mV for triarylcarbenium salts) and in the reduction peak potentials (−23—−311 mV for monoaryl(ferrocenyl)carbenium salts) could be observed as the number of *o*- and *p*-methoxy groups increased. Probably, the electron donation from the *o*- and *p*-methoxy substituents to the central carbon caused the wide negative shift in the redox potentials. These triarylcarbenium salts again showed reversible redox waves in their relatively low concentration region at an ITO electrode in an aqueous acidic medium. In the higher concentration region, an anodic wave was varied to a sharp peak, indicating the adsorption of triarylmethyl radicals. It is very interesting that the reversible redox behavior of these triarylcarbenium salts was observable even in an aqueous medium.

The primary process of plant photosynthesis consists of several electron-transport components. In the electron-transport system, the difference in the redox potentials of the components, and the distance and relative orientation between the redox centers are strictly defined to achieve the conversion of solar energy with high quantum efficiency.[1] Although we have, therefore, to pay attention to these factors in constructing a multistep electron-transfer system, it is not easy even to control the redox potential of some redox components over a wide range. In addition, much attention has also been focused on multistep redox systems because of their special properties, such as conductivity and organic ferromagnetism.[2] It is thus of interest to construct stable multistep redox systems by combining some redox centers, and to examine how the redox properties would be changed.

During the course of our study of 2,6-dimethoxyphenyl derivatives, we attempted the synthesis of di- and triarylcarbenium salts, and mono- and diaryl(ferrocenyl)carbenium salts having some methoxy substituents on the phenyl group,[3—8] and found that the number and position of methoxy substituents on the phenyl group remarkably influences the stability and reactivity of these compounds. For example, bis(2,4,6-trimethoxyphenyl)carbenium perchlorate is recrystallizable even from methanol, and triarylcarbenium salts bearing at least four *o*-methoxy groups are highly stable even in secondary alcohol such as 2-propanol and water. Since these carbenium salts are highly colored, and the characteristic absorption bands are observed in the visible spectrum, utilization as a photosensitizer is also expected. In addition, we have recently reported[9] on the preparation and some physicochemical properties of aryl(ferrocenyl)methanols and related ferrocenyl derivatives. The wide range of cathodic shifts in the redox potentials based on the ferrocene-ferrocenium redox couple could be observed as the number of *o*-methoxy groups increased. We report here on the effect of the number and position of the methoxy substituents on the phenyl group in tri- and diarylcarbenium salts on the redox potentials, prior to constructing multistep redox system. We abbreviate here some methoxyphenyl groups as Φ's, as shown in Scheme 1.



Scheme 1.

Experimental

Tri- and diarylcarbenium salts ([Φ_3C]ClO$_4$, [$\Phi'\Phi^b{}_2C$]ClO$_4$, [FcCΦPh]ClO$_4$, [$\Phi^a{}_2CH$]ClO$_4$, and [FcCΦH]ClO$_4$ [$\Phi, \Phi' = \Phi^a, \Phi^b, \Phi^c, \Phi^e, \Phi^f$]), were prepared as described elsewhere,[3—9] and were checked by IR, ^{1}H and ^{13}C NMR. These compounds were dissolved in 1,2-dichloroethane containing 0.1 M (M = mol dm^{-3}) tetrabutylammonium perchlorate. For a measurement in aqueous solution, the corresponding triarylmethanols were dissolved in 0.1 M HCl to form triarylcarbenium chloride, because triarylcarbenium perchlorates hardly dissolved in 0.1 M HCl. Dissolved oxygen in these solutions was removed by bubbling argon for 20 min before electrolysis. Cyclic voltammetric measurements were then performed at 25 °C in a conventional three-electrode cell with Pt wire (ϕ 0.3 mm×5 mm length) or an indium tin oxide (ITO) (5×5 mm^2, R = 10 Ω cm^{-2}) working electrode, a platinum plate counter electrode, and an aqueous Ag/AgCl reference electrode. Voltammograms were recorded with a Hokuto Denko Model HA-501 potentiostat and a Function Generator HB-104 in connection with a Rika Denki RW-21T X-Y recorder. The formal redox potentials of these compounds were estimated as the midpoint between the anodic and cathodic peak potentials.

Results and Discussion

All of triaryl-type carbenium salts showed reversible redox waves at a Pt electrode in 1,2-dichloroethane, while the reduction of diaryl-type carbenium salts proceeded irreversibly, as typically shown in Fig. 1. In addition, the linear relationships of the cathodic peak current to the square root of the potential sweep rate and to the concentration of the tested arylcarbenium salts were observed, while the cathodic peak potentials were approximately kept constant when varying the sweep rate and concentration, as typically shown in Fig. 2 for $\Phi^b{}_3C^+$. It is evident that the observed waves are due to the reduction of these arylcarbenium salts, and that the mass-transfer rates are governed by the diffusion of these salts to the electrode surface. Since the oxidation of ferrocene is known to proceed with one-electron transfer,[10] the number of electrons transferred in the reduction of these salts can be determined by comparing both specific limiting currents[11] for ferrocene oxidation and the reduction of these salts. Table 1 gives a comparison of the specific limiting currents. The results suggest that the reduction of these salts proceeds with a one-electron transfer to form the corresponding arylmethyl radicals. Also, the thus-formed triarylmethyl radicals seem to be stabilized by a steric effect of Φ-groups, whereas the diarylmethyl radicals are unstable. This presumption is qualitatively supported by a result for constant potential electrolysis of $\Phi^b{}_3C^+$ at −100 mV vs. aq Ag/AgCl with 1.5 F mol^{-1} of quantity of electricity. The electronic spectrum of $\Phi^b{}_3C^+$ in 1,2-dichloroethane showed a strong band with λmax at 524 nm, while that for the solution after electrolysis showed a new band at 370 nm instead of the disappearance of the 524 nm absorption, as shown in the lower part of Fig. 3. On the other hand, the chromium(II) ion reduction of $\Phi^b{}_3C^+$ leads to the formation of tris(2,6-dimethoxyphenyl)methyl radical,[12] and the electronic spec-

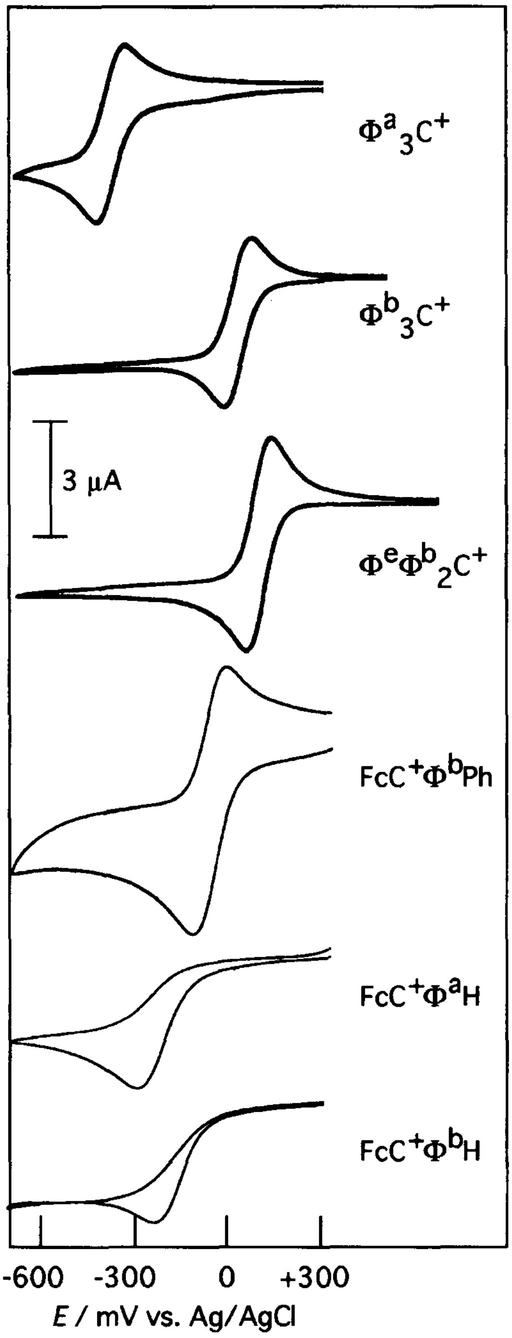


Fig. 1. Typical cyclic voltammograms of arylcarbenium salts at a Pt electrode. A cyclic voltammetric measurement was done at 25 °C. Concentration of the salts was 1 mM in 1,2-dichloroethane containing 0.1 M tetrabutylammonium perchlorate. Potential sweep rate was 20 mV s^{-1}.

Table 1. Value of *n* for Reduction of Carbenium Salts

Compound	*ipc* / *μ* A	*n*
Ferrocene	7.10	1
FcC$^+\Phi^a$H	4.00	ca. 1
Ph$\Phi^b{}_2C^+$	3.73	ca. 1
$\Phi^f\Phi^b{}_2C^+$	3.68	ca. 1
$\Phi^e\Phi^b{}_2C^+$	3.00	ca. 1
$\Phi^b{}_3C^+$	3.20	ca. 1
$\Phi^a{}_3C^+$	3.65	ca. 1

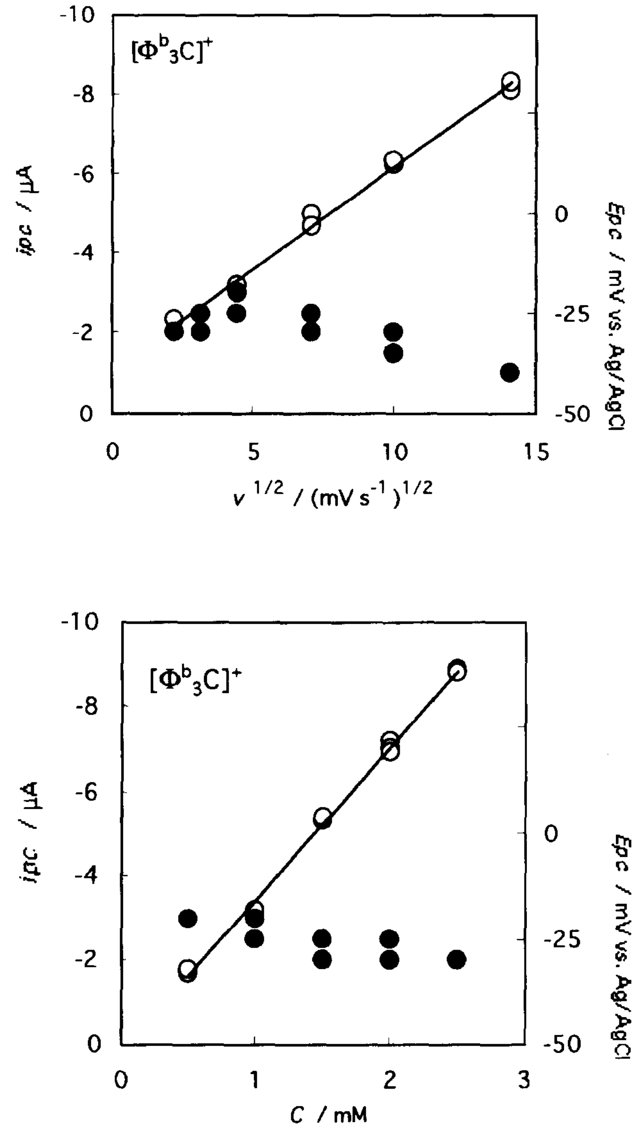


Fig. 2. Relationships of cathodic peak currents and potentials for $\Phi^b{}_3C^+$ to the square root of the potential sweep rate (upper) and to the concentration of $\Phi^b{}_3C^+$ (lower). Symbols in the figure, ○ and ●, represent the values of the cathodic peak current and potential, respectively. The experimental conditions were the same as those in Fig. 1, except that the potential sweep rate (upper) and the concentration of $\Phi^b{}_3C^+$ (lower) were varied.

trum showed a band at 370 nm, as also shown in the upper part of Fig. 3. In addition, the contamination of oxygen into the solution during the electrolysis seems to require an excess quantity of electricity, because it is reported[12] that exposure of the radical solution to air has resulted in a decrease and eventual disappearance of the 370 nm band. In fact, exposure of the decolorized electrolytic solution to air led to the development of a deep-purple color with λmax at 524 nm, due to regeneration of the carbenium salt.

The redox potential of triarylcarbenium salts and the reduction peak potential of monoaryl(ferrocenyl)carbenium salts are summarized in Table 2. A wide range of the cathodic shift in the redox potentials (198—−377 mV vs. aq Ag/AgCl for triarylcarbenium salts) and in the reduction peak potentials (−23—−311 mV vs. aq Ag/AgCl for monoaryl(ferrocenyl)carbenium salts) could be observed as the number of *o*- and *p*-methoxy groups increased, in contrast to the results[9] that the redox potentials of aryl(ferrocenyl)methanes and -methanols based on a ferrocene-ferrocenium redox couple were only affected by the number of *o*-methoxy substituents. However, because this table is somewhat complicated, we will visualize the potential data at a Pt electrode in 1,2-dichloroethane for a further discussion in the relation to the number of methoxy substituents on the phenyl group.

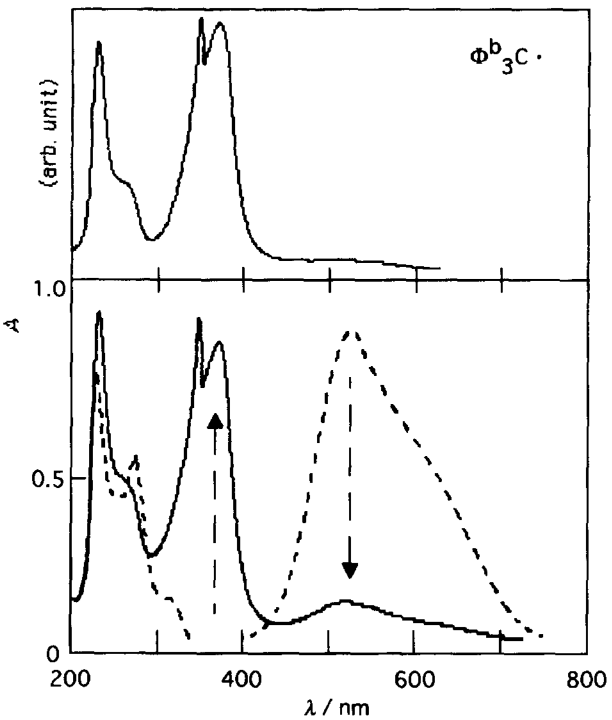


Fig. 3. UV-vis spectra. The dotted and solid lines in the lower figure show the spectra for 50 μM $\Phi^b{}_3C^+$ in 1,2-dichloroethane containing 5 mM tetrabutylammonium perchlorate and for the solution after electrolysis at −100 mV with 1.5 F mol^{-1}, respectively. The upper figure shows the spectrum of 1,2-dichloroethane solution of independently prepared tris(2,6-dimethoxyphenyl)methyl radical with the chromium(II) ion reduction of $\Phi^b{}_3C^+$.

Figure 4 shows the effect of the number of methoxy substituents on the redox potential of triarylcarbenium salts and the reduction potential of monoaryl(ferrocenyl)carbenium salts. A wide range of the cathodic shift over 575 mV could be observed for a series of triarylcarbenium salts. Probably, the electron donation from the *o*- and *p*-methoxy substituents to the central carbon causes the wide negative shift in the redox potentials, i.e., an elevation of the LUMO level of carbenium salts, while the electron donation from only the *o*-methoxy substituent to the ferrocenyl iron is predominant to destabilize the HOMO level of aryl(ferrocenyl)methanes and -methanols.[9]

In addition, the redox potential of $FcC^+\Phi^bPh$ and the reduction potentials of $FcC^+\Phi^aH$ (−86 and −311 mV) were observed at much lower potentials than those of $Ph\Phi^b{}_2C^+$

Table 2. Redox Potentials of Tri- and Diarylcarbenium Salts

	No of MeO	$E^{\circ a)}$	$Epc^{b)}$	$\Delta Ep^{c)}$	$E^{\circ a)}$	$\Delta Ep^{c)}$	$E^{\circ a)}$	$\Delta Ep^{c)}$
Compound		at Pt in 1,2-dichloroethane			at ITO in 1,2-dichloroethane		at ITO in 0.1 M HCl	
$\Phi^{a}{}_{3}C^{+}$	9	−377		93	−396	132	−353	235
$\Phi^{a}\Phi^{b}{}_{2}C^{+}$	7	−212		90				
$\Phi^{b}{}_{3}C^{+}$	6	21		88	14	128	−61	82
$\Phi^{f}\Phi^{b}{}_{2}C^{+}$	5	25		94	10	140	−290	70
$\Phi^{e}\Phi^{b}{}_{2}C^{+}$	5	97		100	82	117	−23	65
$Ph\Phi^{b}{}_{2}C^{+}$	4	198		95	186	129	53	70
$Ph^{3}C^{+d)}$					346	129		
$\Phi^{a}{}_{2}C^{+}H$	6		−210					
$FcC^{+}\Phi^{b}Ph$	2	−86		105				
$FcC^{+}\Phi^{a}H$	3		−311					
$FcC^{+}\Phi^{b}H$	2		−210					
$FcC^{+}\Phi^{e}H$	1		−142					
$FcC^{+}\Phi^{c}H$	2(1)$^{e)}$		−132					
$FcC^{+}PhH$	0		−23					

a) Redox potential in mV vs. Ag/AgCl. b) Cathodic peak potential when irreversible in mV vs. Ag/AgCl. c) Potential difference between anodic and cathodic peaks. d) Since this compound is unstable in 1,2-dichloroethane, 1,2-dichloroethane solution of triphenylmethanol was acidified with trifluoroacetic acid to form the corresponding carbenium salt, and was subjected to a cyclic voltammetric measurement without further purifications. Similar redox potential was reported by Arnett et al.[13] at a glassy carbon in sulfolane/3-methylsulfolane. e) One of methoxy groups is at *meta*-position.

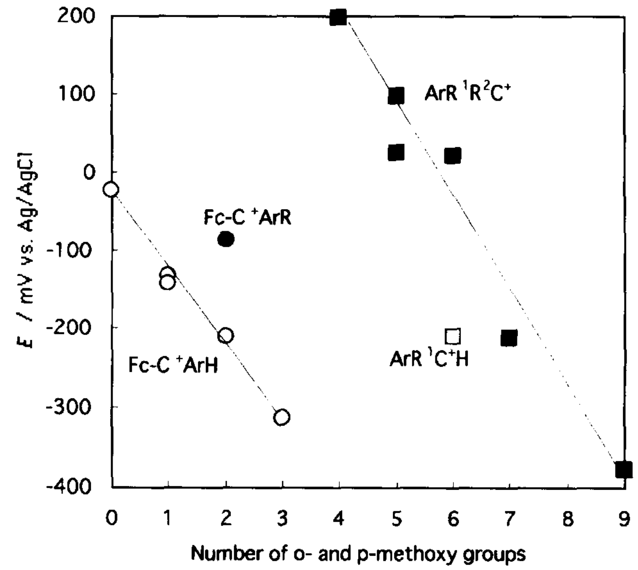


Fig. 4. Effect of the number of methoxy substituents on the redox potentials. The experimental conditions were the same as those in Fig. 1.

and $\Phi^{a}{}_{2}C^{+}H$ (198 and −210 mV). The substitution of the Φ-groups to the Fc-group results in a change in the reduction potentials to the negative direction; that is, the Fc-group is more highly effective in determining the redox potentials than the Φ-groups. This result is of great interest in view of constructing multistep redox systems by combining some redox centers, because oxidation-reduction of the Fc-group generally proceeds with a reversible one-electron transfer;[10] in addition, it becomes easier to control the redox potential of the redox centers. Cyclic voltammetric measurements were therefore conducted in order to obtain further detailed redox behavior of aryl(ferrocenyl)carbenium salts based on a ferrocene–ferrocenium redox couple. An anodic wave due to ferrocene oxidation appeared at around 1.3 V vs. aq Ag/AgCl for the six aryl(ferrocenyl)carbenium salts listed in Table 2, but no cathodic counterpart corresponding to this peak was found even at a higher potential sweep rate. Instead, a few small cathodic peaks appeared at around 0.8—0.9 V (detailed data and cyclic voltammograms not shown). That is, the oxidation of the Fc-group in aryl(ferrocenyl)carbenium salts proceeds irreversibly, although the reason is not clear at the present stage. Moreover, the oxidation potentials were observed at an extremely higher potential than those of aryl(ferrocenyl)methanes and -methanols.[9] These results may be understood by suggesting that the central cationic carbon of the carbenium salts is electron-withdrawing from the Fc-group.

Since all of the triaryl-type carbenium salts showed reversible redox waves at a Pt electrode in 1,2-dichloroethane, the redox behavior of these triarylcarbenium salts was examined at an optically transparent ITO electrode in 1,2-dichloroethane, in view of constructing multistep redox systems induced by the illumination of light. A typical cyclic voltammogram of $\Phi^{b}{}_{3}C^{+}$ is shown in Fig. 5. All of the triarylcarbenium salts again showed reversible redox waves, although the reversibility was somewhat lowered than that at a Pt, perhaps due to an increase in the electrode surface resistance. The redox potentials are also listed in Table 2. The redox behavior of triarylcarbenium salts was quite similar to that at Pt, and the redox potentials were widely shifted to the negative direction as the number of methoxy substituents increased.

We have reported[4] that $\Phi^{b}{}_{3}C^{+}$, $\Phi^{e}\Phi^{b}{}_{2}C^{+}$, and $Ph\Phi^{b}{}_{2}C^{+}$ were inert in 1,2-dichloroethane at ambient temperature. In addition, $\Phi^{b}{}_{3}C^{+}$ was stable toward hydrolysis, even in hot 2-propanol at 60 °C for 12 h. We have thus tried to examine the redox behavior of these triarylcarbenium perchlorates at an ITO electrode in an aqueous medium acidified with hy-

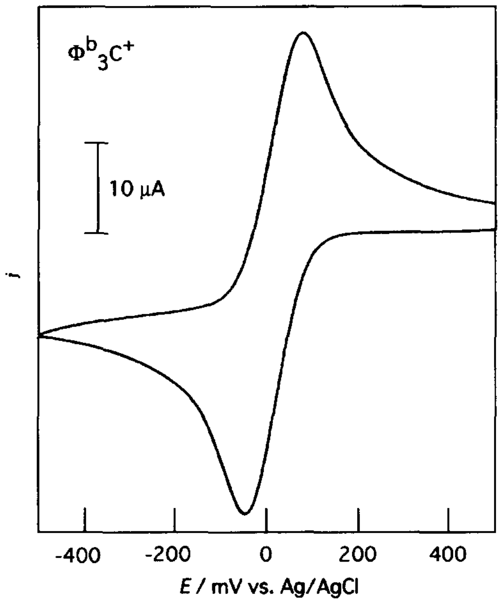


Fig. 5. Typical cyclic voltammogram of $\Phi^{b}{}_{3}\mathrm{C}^{+}$ at an ITO electrode in 1,2-dichloroethane. A cyclic voltammetric measurement was done at 25 °C. Concentration of the salt was 1 mM in 1,2-dichloroethane containing 0.1 M tetrabutylammonium perchlorate. Potential sweep rate was 20 mV s^{-1}.

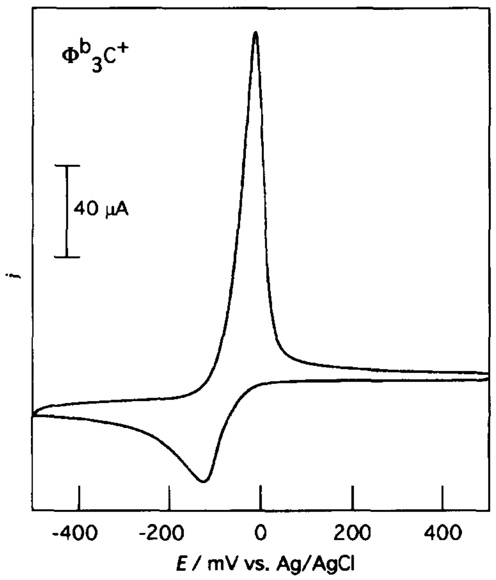


Fig. 6. Typical cyclic voltammogram of $\Phi^{b}{}_{3}\mathrm{C}^{+}$ at an ITO electrode in 0.1 M aqueous HCl. A cyclic voltammetric measurement was done at 25 °C. Concentration of the salt was 0.5 mM in 0.1 M aq HCl. Potential sweep rate was 200 mV s^{-1}.

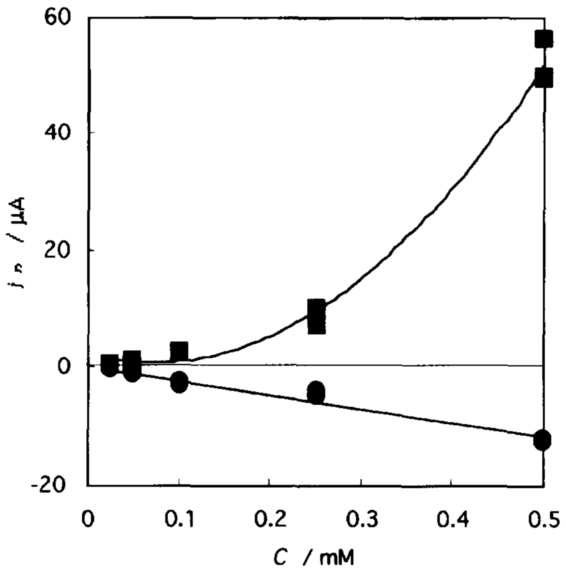


Fig. 7. Relationship of cathodic and anodic peak currents to the concentration of $\Phi^{b}{}_{3}\mathrm{C}^{+}$. Symbols in the figure, ■ and ●, represent the values of the anodic and cathodic peak currents, respectively. The experimental conditions were the same as those in Fig. 6, except that the potential sweep rate was 20 mV s^{-1}.

drochloric acid. But, these salts were poorly soluble in an acidic medium. The corresponding triarylmethanols were therefore dissolved in 0.1 M HCl to form triarylcarbenium chloride[4—6] for a measurement in aqueous solution. All of the tested triarylcarbenium salts showed reversible redox waves in their relatively low concentration region (for example, a cyclic voltammogram of 0.1 mM $\Phi^{b}{}_{3}\mathrm{C}^{+}$ showed typically reversible, diffusion-controlled redox waves), just as those at an ITO electrode in 1,2-dichloroethane. However, in the higher concentration region, the cyclic voltammogram was slightly different in shape; that is, the anodic wave was gradually varied to a sharp peak, as typically shown in Fig. 6. Although a linear relationship of the cathodic peak current to the concentration of triarylcarbenium salts was observed, the anodic peak current steeply increased with increasing the concentration, as shown in Fig. 7. In addition, the cathodic peak potentials were approximately kept constant when varying the concentration of triarylcarbenium salts, while the anodic peak potentials were shifted to about 50 mV positive above 0.3 mM of concentration region (data not shown). These results suggest that the triarylmethyl radicals formed from the corresponding carbenium salts with one-electron reduction were adsorbed on the electrode surface because of their lower solubility into the aqueous acidic medium. However, a better linear relationship was obtained between the anodic peak current and the square root of the potential sweep rate (0.971 of the correlation coefficient), rather than the direct sweep rate itself (0.938), as shown in Fig. 8. Thus, the anodic wave may be controlled by diffusion of the carbenium ion from the electrode surface.

A cathodic shift in the redox potentials could be observed as the number of *o*- and *p*-methoxy groups increased, the result being also summarized in Table 2. $\Phi^{f}\Phi^{b}{}_{2}\mathrm{C}^{+}$ has not shown a redox potential at the position expected from Table 2 (about −60 mV). Instead, a redox couple was observed at −290 mV with 70 mV of ΔEp. The redox potential was in an extremely more negative region than the expected value. We have already reported[5] that triarylmethanol, $\Phi^{f}\Phi^{b}{}_{2}\mathrm{COH}$, reacts with acids in a variety of solvents to give triarylcarbenium salts, $\Phi^{f}\Phi^{b}{}_{2}\mathrm{CX}$, (4-$\mathrm{HOC_6H_4}$)$\Phi^{b}{}_{2}\mathrm{CX}$, or 4-

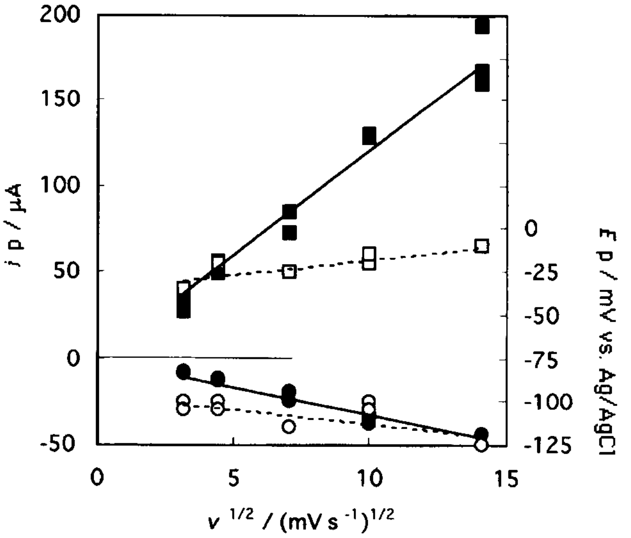


Fig. 8. Relationship of cathodic and anodic peak currents, and potentials to the square root of the potential sweep rate. Symbols in the figure, ■, ●, □, and ○, represent the values of the anodic and cathodic peak currents, and potentials, respectively. The experimental conditions were the same as those in Fig. 6, except that the potential sweep rate was varied.

bis(2,6-dimethoxyphenyl)methylene-2,5-cyclohexadienone, $O{=}C_6H_4{=}C\Phi^{b}_{2}$, depending on the conditions. Thus, the redox couple at −290 mV seems to be attributable to oxidation-reduction of the above-mentioned *p*-quinomethane. In fact, independently synthesized $O{=}C_6H_4{=}C\Phi^{b}_{2}$ showed a redox wave at the same potential (data not shown). In addition, the redox potentials observed in an aqueous medium (−61, −23, and 53 mV for $\Phi^{b}_{3}C^{+}$, $\Phi^{e}\Phi^{b}_{2}C^{+}$, and $Ph\Phi^{b}_{2}C^{+}$, respectively) were much lower than those in 1,2-dichloroethane (14, 82, and 186 mV). Nevertheless, the redox potential for $\Phi^{a}_{3}C^{+}$ in aqueous acidic media shifted in the positive direction to −353 mV from −396 mV in 1,2-dichloroethane. We have recently reported[6] that when 1 M NaOH was added to a hot 1 M HCl solution of $\Phi^{a}_{3}COH$, 4-bis(2,4,6-trimethoxyphenyl)methylene-3,5-dimethoxy-2,5-cyclohexadienone was formed, similarly to that observed for $\Phi^{f}\Phi^{b}_{2}COH$.[5] Thus, the redox wave may also be due to the oxidation-reduction of the *p*-quinomethane, and the negative shift in the redox potentials from −290 to −353 mV seems to be due to an electron-donating effect from methoxy substituents on the *p*-quinomethane. In any case, it is very interesting that the reversible redox behavior of these triarylcarbenium salts ($\Phi^{b}_{3}C^{+}$, $\Phi^{e}\Phi^{b}_{2}C^{+}$, and $Ph\Phi^{b}_{2}C^{+}$) was observable even in an aqueous medium. An attempt to modify these carbenium salts onto an ITO electrode surface in the above-mentioned manner and their photoelectrochemical measurements in an aqueous medium are in progress.

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